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CHARACTERIZATION AND REACTIVITY
OF
ISOCYANIDE COMPLEXES OF MANGANESE

BY

HANS JUERGEN MUEH

A thesis submitted in partial fulfillment of the
requirements for the degree of

DOCTOR OF PHILOSOPHY
(Chemistry - Inorganic)

at the

UNIVERSITY OF WISCONSIN
Madison, Wisconsin

1976

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CHARACTERIZATION AND REACTIVITY OF ISOCYANIDE COMPLEXES OF MANGANESE

(Abstract)

By Hans Juergen Mueh
Captain, USAF

UNIVERSITY OF WISCONSIN-MADISON
1976

DOCTOR OF PHILOSOPHY

(169 Pages)

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A series of complexes $\text{Mn}(\text{RNC})_6^{(+)}$ (R = a monosubstituted phenyl ring) were prepared by reaction of MnI_2 or $\text{Mn}(\text{CO})_5\text{X}$ (X = Cl, Br) with the free ligand. The E_1 values of the complexes for the $1e^-$ oxidation from $+1 \rightarrow +2$ were correlated with the Hammett σ_p of the substituent group and a correlation coefficient of 0.98 was obtained.

Attempted oxidation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ with AgPF_6 in THF resulted in the preparation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6^{(+)}\text{PF}_6^{(-)}$. The complex $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ reacted with AgPF_6 in a series of complexing solvents, producing the complexes $(\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L}))\text{PF}_6$ (L = p-CH₃C₆H₄NC, C₅H₅N, CH₃NC, (CH₃)₃CNC, and o-CH₃C₆H₄NH₂). A plot of E_1 vs $\nu(\text{CO})$ for these complexes produced a correlation coefficient of 0.99₁ and is consistent with the range of π -acceptor strengths of L.

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The replacement of bromide ion in $\text{Mn}(\text{CO})_{5-n}(\text{CH}_3\text{NC})_n\text{Br}$ ($n = 2, 3, 4$) by CO and CH_3NC , accomplished in the presence of the halogen acceptors AlCl_3 (CO reactions only) or AgPF_6 , is found to be stereospecific, thus providing routes to the pure isomeric complexes cis- and trans- $(\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_4)^{+}$ and fac- and mer- $(\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_3)^{+}$. E_1 values for the isomeric species differ substantially. The qualitative explanation for the difference is justified by molecular orbital calculations.

→ Ultraviolet irradiation of $\text{CpMn}(\text{CO})_3^+$ in THF with excess isocyanide produced the complexes $\text{CpMn}(\text{RNC})_3$ ($\text{R} = \text{CH}_3$, C_6Cl_5 , C_6H_5 , p- ClC_6H_4). The E_1 values vary consistently with the known range of π -acceptor strengths of the isocyanides.

→ A series of complexes $\text{Mn}_2(\text{CO})_{(10-x)}(\text{RNC})_x$ ($x = 1, 2, 4, 5$; $\text{R} = \text{CH}_3$, C_6H_5 , p- ClC_6H_4) was prepared thermally and by nucleophilic attack of $\text{Mn}(\text{CO})_{(5-x)}(\text{RNC})_x$ with $\text{Mn}(\text{CO})_5^+$.

Mass spectral studies showed evidence of stepwise loss of carbonyl, α -cleavage of the isocyanide, ligand rearrangement, and protonation of the complexed isocyanide.

→ The complexes $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{SnCl}_3$) were also prepared and examined electrochemically. The E_1 values are consistent with the variation of electron withdrawing ability of the X group.

* were synthesized

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CHAPTER I

CORRELATION OF $E_{1/2}$ VALUES WITH HAMMETT σ 's OF
SOME PARA AND META SUBSTITUENTS OF ARYL
ISOCYANIDE COMPLEXES OF THE TYPE $[\text{MnL}_6]\text{PF}_6$

A. INTRODUCTION

Several researchers have investigated octahedral complexes of the type $M(CO)_{6-x}(L)_x^y$ to determine the effect of varying the type and number of ligand L on various physical and chemical properties. Of these, only a few have examined the electrochemical behavior of isocyanide derivatives of octahedral complexes.

McCleverty and coworkers¹ prepared a series of isocyanide complexes $M(CO)_{6-x}(CNR)_x$ ($x = 1-3$; $M = Cr, Mo$; $R = Me, Et, Pr^i, C_6H_{11}, Bu^t, p\text{-tolyl}, C_6H_5,$ and $p\text{-ClC}_6H_4$) and employed spectroscopic (infrared, ultraviolet, mass spec, and nmr data) and electrochemical measurements to assess the effect of varying R and x on the nature of the bonding in these systems.

The electrochemical measurements showed that within a given series of isocyanide complexes varying only in their alkyl substituents, there is no significant difference in $E_{1/2}$ values, suggesting that alkyl isocyanide ligands are "electronically" alike. Among the aryl isocyanide complexes, there was a marked difference in $E_{1/2}$ values between similar species $M(CO)_{6-x}(RNC)_x$, ($M = Cr, Mo$) in which R is either $p\text{-CH}_3C_6H_4$ or $p\text{-ClC}_6H_4$, which was attributed to the inductive and/or mesomeric effects of

the para-substituents on the benzene rings.

A later reference by Treichel and Dirreen² examined the electrochemical oxidations of several aryl isocyanide complexes of the type $\text{Cr}(\text{RNC})_6$ and $\text{Mn}(\text{RNC})_6^+$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$) and noted small, though significant, differences in oxidation potentials depending on the nature of the para-substituent group. Predictably, electron-donor groups were seen to lower the oxidation potential while electron-withdrawing groups made the complexes more difficult to oxidize. Concurrent with the work discussed here the series of chromium-aryl isocyanide complexes was extended by Treichel and Essenmacher³ and the same correlation of ring substituent with $E_{1/2}$ values was extended and further defined.

We also decided to extend the series of manganese-aryl isocyanide complexes, $\text{Mn}(\text{RNC})_6^+$, in which the R group represents a phenyl ring mono-substituted with a wider range of donating and withdrawing groups than those previously reported. By having a larger sampling of species to compare, we hoped to obtain some quantitative relationship between the variation in $E_{1/2}$ values and the electronic properties of the substituent.

Researchers have attempted to correlate electronic substituent effects with carbonyl stretching frequencies

and force constants. Fischer¹² recognized the existence of a qualitative relationship between $\nu(\text{CO})$ and Hammett σ (σ_p) values for a large number of tricarbonylchromium-complexed benzene derivatives. More quantitative linear correlations between $k(\text{CO})$, the CO stretching force constant, and σ_p values for selected complexes have subsequently been derived.¹³⁻¹⁶ More recently, Neuse¹⁷ established quantitative correlations between selected σ substituent parameters and the carbonyl stretching force constant for 28 substituted tricarbonylchromium-complexed arene compounds. An earlier paper by Treichel and Stewart¹⁸ reported carbonyl stretching frequencies for several meta- and para- $\text{XC}_6\text{H}_4\text{Mn}(\text{CO})_5$ complexes and found them little affected by nature or position of the substituent group on the ring. They concluded, therefore, that π -bonding effects between ring and metal are relatively insignificant.

In light of more recent research¹⁹ we propose to extend the correlation with σ parameters one step further, by relating the constants to the $E_{1/2}$ values of the $\text{Mn}(\text{RNC})_6^+$ complexes. A paper by Fenske and Sarapu,¹⁹ which examined the bonding properties of the complexes

$\text{Mn}(\text{CO})_{5-n}(\text{CH}_3\text{NC})_n\text{Br}$ ($n = 0-4$) and $\text{Mn}(\text{CO})_{6-n}(\text{CH}_3\text{NC})_n^+$ ($n = 0-6$), presented several interesting conclusions which suggest that this correlation can be made. It was found, on the basis of force constant analyses, that the carbonyl and isocyanide force constants are linearly related to the total electron occupations of the respective σ and π ligand orbitals. Furthermore, an examination of the calculations reveals that the stabilization of the highest occupied molecular orbital (HOMO) is also a direct function of the electron distribution within the ligand moieties. Finally, the oxidation potentials of the species investigated ($E_{1/2}$ values) were found to be linearly related to the HOMO energies. Thus, in light of the linear correlation previously established between σ parameters and carbonyl force constants, $k(\text{CO})$, and the correlation of force constants with HOMO energies and $E_{1/2}$ values established by Fenske and Sarapu,¹⁹ it is reasonable to expect a similar linear correlation of σ parameters with $E_{1/2}$ values.

During the course of our investigations we also noticed the invariance of $\nu(\text{CN})$ to the substantial range of σ parameters and $E_{1/2}$ values for the $\text{Mn}(\text{RNC})_6^+$ complexes. In an attempt to explain this phenomenon, a joint project was initiated in conjunction with the theoretical

inorganic research group of Dr. Richard F. Fenske. Preliminary MO calculations on free ligands and fictional isocyanide compounds were carried out by Bruce Bursten and the initial results are presented herein.

In addition, we attempted to apply the relationship recently reported by Pickett and Pletcher²⁰ to our $\text{Mn}(\text{RNC})_6^+$ and to the $\text{Cr}(\text{RNC})_6$ complexes also prepared in our group³ to examine the usefulness of the relationship. The equation is presented as follows:

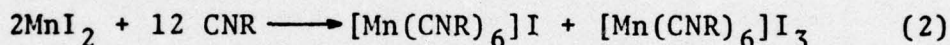
$$E^\circ = A + x(dE^\circ/dx)_L + 1.48y \quad (1)$$

A is a constant dependent on the solvent and the reference potential; (dE°/dx) is a parameter characteristic of the ligand, L, which defines the shift in E° caused by the replacement of one CO ligand by one molecule of L. In attempting to employ this equation, we noted several shortcomings and will use this opportunity to analyze the relationship in depth and suggest ways to improve its predictive capability.

Finally, in preparing this series of $\text{Mn}(\text{RNC})_6^+$ complexes, different synthetic approaches were employed. It was found that the most favorable choice of reaction depends to a considerable extent on the nature of the ligand. A discussion of reactions is also presented herein.

B. RESULTS AND DISCUSSION

In the course of our work, we employed a variety of synthetic methods to prepare the Mn(RNC)_6^+ complexes. Sacco²¹ was the first to recognize that anhydrous manganese(II) iodide behaves differently from other manganous salts in reactions with isocyanides. This compound was found to react with alkyl and aryl isocyanides by the following equation:



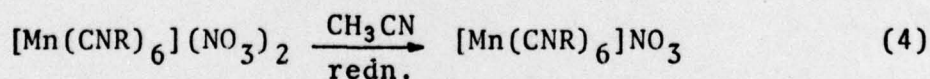
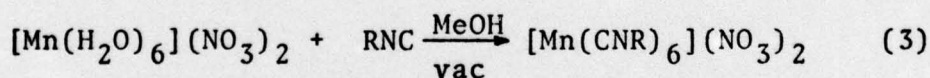
Interestingly, the complex $[\text{Mn(CNR)}_6]\text{I}_3$ is a triiodide of hexaisocyanide manganese(I). In the case where R = alkyl, the iodide is usually too soluble to obtain it in pure form from the original solution, so the reaction mixture is routinely reacted with excess iodine to fully convert the mixture to the triiodide which is recovered, purified, and then shaken with aqueous sodium thiosulphate to convert back to the iodide. The triiodide is converted to the iodide because its solubility in all common solvents is too low for further synthetic and analytical use. In our reactions of MnI_2 with various aryl isocyanides, we find that addition of free iodine is unnecessary. The crude reaction mixture is first evaporated to dryness, then taken up in dichloromethane, filtered to remove insol-

uble salts and decomposition products, and shaken with an aqueous sodium thiosulphate solution. In most cases, this produces a noticeable lightening in color as the triiodide is converted to the iodide. For our electrochemical measurements, the iodide salt is inappropriate because the iodide ion complicates the analysis by exhibiting several redox reactions at moderate applied potentials. For this reason, we routinely converted all of the iodide salts to the hexafluorophosphate salts by taking the iodide up in warm ethanol and treating the solution with excess ammonium hexafluorophosphate, NH_4PF_6 , which then precipitates the less soluble PF_6^- salt.

It should be noted that several $\text{Mn}(\text{CNR})_6^+$ complexes were prepared only with difficulty and in generally poor yield by Sacco's²¹ method. We therefore examined other possible methods of preparation. Joshi, Pauson and Stubbs²² noted the formation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6^+$ in the reaction of $\text{Mn}(\text{CO})_5\text{Cl}$ with phenyl isocyanide in refluxing tetrahydrofuran. A subsequent paper by Treichel²³ and coworkers presented a more definitive study of reactions of phenyl isocyanide with $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) and found that $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{X}$ complexes could be prepared invariant to the halide. Interestingly, we noted in our investigations

that the Mn(RNC)_6^+ complexes which proved to be difficult to prepare by reaction of free ligand with MnI_2 could be obtained in relatively high yield (20-50%) when the isocyanide was reacted with $\text{Mn(CO)}_5\text{Cl}$ or $\text{Mn(CO)}_5\text{Br}$. Of particular note are the complexes $[\text{Mn(m-CF}_3\text{C}_6\text{H}_4\text{NC)}_6]\text{PF}_6$ and $[\text{Mn(p-NO}_2\text{C}_6\text{H}_4\text{NC)}_6]\text{PF}_6$.

The species $[\text{Mn(m-CF}_3\text{C}_6\text{H}_4\text{NC)}_6]\text{PF}_6$ was recovered in a poor 5% yield by Sacco's method, while reaction with $\text{Mn(CO)}_5\text{Cl}$ in refluxing THF for ~7 hours produced a 20% yield of the complex. The formation of the complex $[\text{Mn(p-NO}_2\text{C}_6\text{H}_4\text{NC)}_6]\text{PF}_6$ deserves special mention. The species was first reported in a paper by Bailey and Marshall²⁴ which discusses the preparation of a series of aryl isocyanide complexes by reaction of hexaaquomanganese(II) nitrate, $\text{Mn(NO}_3)_2 \cdot 6\text{H}_2\text{O}$, with the free ligand in methanol under vacuum.

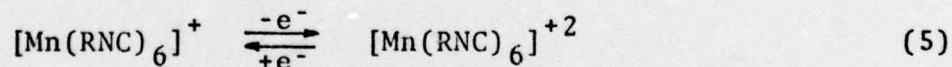


We tested the utility of this reaction by attempting to prepare $[\text{Mn(p-IC}_6\text{H}_4\text{NC)}_6]\text{NO}_3$ and $[\text{Mn(p-NO}_2\text{C}_6\text{H}_4\text{NC)}_6]\text{NO}_3$. After several unsuccessful attempts, we finally isolated a small amount (1% yield) of $[\text{Mn(p-NO}_2\text{C}_6\text{H}_4\text{NC)}_6]\text{NO}_3$, but

only after prolonged pumping at much lower pressures (10^{-3} - 10^{-4} torr) than that reported by Bailey and Marshall (0.1 - 0.2 torr). As a result, we decided to attempt to prepare the complex $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$ by the methods we have previously mentioned. After many unsuccessful attempts at reacting MnI_2 with the ligand in ethanol, we ran the reaction in refluxing THF for ~3 hours, treated the solution with NH_4PF_6 , removed the THF, and washed the residue successively with CCl_4 , H_2O , ethanol, and CH_3CN . The dark orange product, which is partially soluble in acetone, exhibits infrared absorptions in that solvent consistent with an MnL_6^+ complex ($2090\text{ cm}^{-1}(\text{s})$, $2070\text{ cm}^{-1}(\text{m})$). Assuming total conversion to the PF_6^- salt, the complex was isolated in 27% yield. Its low solubility made purification difficult, a problem also noted by Bailey and Marshall.²⁴ In an attempt to improve the yield of this complex, we eventually reacted the ligand with $\text{Mn}(\text{CO})_5\text{Br}$ in refluxing THF for ~48 hours and recovered a dark orange precipitate assumed to be $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{Br}$ in 43% yield. The complex was then partially converted to the PF_6^- salt by refluxing in acetone in the presence of NH_4PF_6 . The resulting product exhibited the expected $\nu(\text{CN})$ (2090 cm^{-1} , 2070 cm^{-1}) and $\nu(\text{PF})$ (840 cm^{-1}) absorptions. Further support for

the formation of the MnL_6^+ complex is given by the isolation of the complex $\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5\text{Br}$ from the THF solution. This complex is discussed in more detail in Chapter VI. Among the other MnL_6^+ complexes prepared, only the species $[\text{Mn}(\text{p-NCC}_6\text{H}_4\text{NC})_6]\text{I}$ exhibited any anomolous behavior. Its low solubility in ethanol led to the use of acetone for metathesis to the PF_6^- salt, and attempts to find the right solvent system to obtain pure crystals finally led to $\text{CH}_3\text{CN-H}_2\text{O}$ as the system of choice.

The cyclic voltammetry of the MnL_6^+ complexes appears to be well-behaved. However, as can be seen by the difference in peak potentials for anodic and cathodic current-potential curves (Table 1), the theoretical difference of 59 mV required for a reversible process is never achieved. Yet the amount of current flowing on oxidation and reduction was the same or nearly so and suggests a simple one-electron transfer process,



Several other researchers have noted this same behavior. Kotz²⁵ and coworkers discussed the electrochemistry of ferrocenylphosphines and their complexes and found the systems to be chemically reversible according to the oxidation and reduction current and controlled potential

coulometry experiments, in which the same number of electrons was lost on oxidation as was gained in re-reduction. In practice, however, the oxidation and reduction peaks routinely exhibited differences greater than 59 mV. Furthermore, a separation of 130 mV was noted for the cyclic voltammetry of ferrocene, a system known to be completely reversible at a solid electrode.²⁶ Also, McCleverty²⁷ and coworkers have reported peak separations of 170 to 230 mV for reversible oxidations of complexes of the type $\text{Cr}(\text{CO})_5\text{L}$ (L = phosphines, amines) in the same solvent used in our work, CH_2Cl_2 . With this in mind, it seems reasonable to conclude, as Kotz²⁵ has done, that solvents and cell design can greatly affect this theoretical reversibility criterion in practice. It seems to us more reasonable, therefore, to place more importance on the appearance of the current-potential curves as they relate to the anodic and cathodic currents. Thus a cyclic voltammetry curve which meets the criterion, $|i_{p,a}| \approx |i_{p,c}|$, has in practice proven to be a more accurate gauge of chemical reversibility and stability of the oxidized or reduced species. The one exception to the well-behaved curves generally exhibited by the MnL_6^+ complexes occurs in the scan of the complex $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$. The complex

could only be partially dissolved in the dichloromethane solvent and the cathodic peak generally disappeared after the first scan apparently due to coating of the platinum electrode possibly caused by the precipitation of the oxidized species.

Once the $E_{1/2}$ values for the complexes were obtained (Table 1), it became obvious that a correlation with the ring substituents exists. We chose the readily available σ constants as the parameters to correlate with our electrochemical data. Hammett's constant, σ_p , is a measure of the total inductive and mesomeric electronic effect exerted by a substituent group onto the detection center.¹⁰ Taft and coworkers⁷ have published data on the ^{19}F nmr shielding in meta- and para-substituted fluorobenzenes, $\text{FC}_6\text{H}_4\text{X}$, which allow the separation of the inductive (σ_I) and resonance (σ_R) effects of the substituent group X. The inductive parameter σ_I measures the relative ability of the substituent to withdraw or release electron density both through space and through the σ -bond system of the benzene ring.¹¹ The resonance parameter σ_R is a measure of the relative ability of the substituent to withdraw or release electron density by a resonance interaction with the benzene π system.¹¹ The substituent X = H is the reference for these constants and is assigned

the value $\sigma_p = \sigma_I = \sigma_R = 0$. We plotted the $E_{1/2}$ values against the σ 's (σ_I , σ_R and σ_p ; Table 1) to find the best correlation. It is immediately obvious that little or no correlation exists between the $E_{1/2}$ values and σ_I parameters. A least squares fit of the data²⁸ produced a correlation coefficient $r = 0.58$. A slightly better correlation coefficient was obtained when $E_{1/2}$ values were plotted against σ_R ($r = 0.71$), the resonance parameter. However, when $E_{1/2}$ is plotted against σ_p , Hammett's constant, the correlation is excellent ($r = 0.98$; Figure 1). These correlations are presented in Table 3; the data include intercept and slope of the regression line, $\sigma = b_0 + b_1 (E_{1/2})$, and the standard deviation of the slope, s .

An examination of the various correlations leads to several important postulations. First, based on the poor correlation of σ_I with $E_{1/2}$, inductive transmission of the electronic effect from the substituent to the metal detection center either through the arene ring's σ framework or through space is not the exclusive mechanism. Second, resonance is also probably not the exclusive mechanism of transmission, as evidenced by the poor correlation established for σ_R . It is apparent, therefore,

that a combination of inductive and resonance effects more closely approaches the correct electronic conveyance mechanism, as evidenced by the correlation established for the total parameter, σ_p .

To insure that we had indeed formed the Mn(RNC)_6^+ complexes by the various methods previously mentioned, we looked for the characteristic, strong $\nu(\text{CN})$ absorption mode expected (T_{1u} in idealized O_h symmetry) by noting the shift in frequency from the free (2120 cm^{-1}) to complexed (2090 cm^{-1}) ligand. Interestingly, the strong absorption at 2090 cm^{-1} is almost invariant to the wide range of σ_p 's (-0.27 for CH_3O^- ; $+0.78$ for $-\text{NO}_2$; Table 1) and $E_{1/2}$ values ($0.81 - 1.31$ volts), quite unlike the linear correlation observed between $\nu(\text{CO})$ and a variety of substituent effects.¹²⁻¹⁷ A recent paper²⁹ approached the subject by presenting a semiempirical MO-LCAO-CNDO investigation of a series of isocyanides, RNC ($\text{R} = \text{CH}_3$, C_2H_5 , C_2H_3 , C_6H_5 , $p\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$), and describing how some properties of free isocyanides determine the spectroscopic behavior of the complexes. It was noted that although the C-N bond orders do not differ appreciably among the various isocyanides, the energy and compositions of the highest occupied molecular orbital (HOMO)

are significantly different. The HOMO orbitals were shown to contain contributions from the atomic orbitals of π -symmetry of the CN group; these contributions decrease when the CN group is conjugated, and more so when extensive delocalization is present. The destabilization of the HOMO is accompanied by an increase in stabilization of the lowest unoccupied molecular orbital (LUMO) and explains why in general the alkyl isocyanides are poorer π -acceptors than the aromatic isocyanides. The paper qualitatively noted the effect of varying the R group (in RNC) on the energy of the orbital (LUMO) which interacts with the d orbitals of the metal, but failed to present a satisfactory explanation for the large shifts in $E_{1/2}$ values (and HOMO energies) vs the invariance of $\nu(\text{CN})$ evident for the substituted aryl isocyanides we prepared.

Therefore, preliminary calculations³⁰ were carried out on a series of free ligands representing a wide range of σ substituents ($p\text{-CNC}_6\text{H}_4\text{X}$; $\text{X} = \text{H}, \text{CH}_3, \text{F}, m\text{-CH}_3, \text{OCH}_3, \text{Cl}, \text{NO}_2$). The LUMO of each of these ligands is a bonding combination of an antibonding orbital on the ring (similar to one of the e_{2u} orbitals in benzene) and an antibonding π^* orbital of the CN fragment. It is primarily local-

ized on the ring but has a significant (~20%) contribution from the CN carbon and for reference will be called a ring- π^* orbital. A corresponding antibonding combination of the same orbitals, located primarily on the CN fragment, is significantly higher in energy and will be called a π^* -ring orbital. Finally, there exists a π^* orbital of the CN fragment which is not of suitable symmetry to interact with the π system of the ring and will be called a π^* orbital. Energetically, these orbitals are ordered as follows: ring- π^* < π^* < π^* -ring. The calculated energy levels for p-CNC₆H₄X ring- π^* , π^* , and π^* -ring orbitals are presented in Table 3. Preliminary calculations were also carried out on the fictional compounds Cr(CNH)₅(p-CNC₆H₄X) (X = H, Cl, CH₃) to determine the effects of an ML₆ ligand environment. The metal atom π -bonds primarily to the ring- π^* and π^* orbitals, the π^* -ring orbital being energetically unfavorable. As seen in Table 3, an electron withdrawing substituent, e.g. NO₂, substantially lowers the ring- π^* level while an electron donating substituent raises it. Since this level is energetically closest to the metal π orbitals, it is expected to be most affected by backbonding. Thus a notably increased backbonding can be expected as electron-withdraw-

ing groups are added; electron donating groups produce the opposite effect. This will cause large fluctuations in the HOMO energy which, as shown in previous studies,³¹ could be reflected in the $E_{1/2}$ values. However, this change in HOMO energy would not be reflected in $v(\text{CN})$ since the ring- π^* orbital is primarily localized on the ring and the first CN π^* orbital is energetically less favorable for backbonding from the metal.

The dependence of $E_{1/2}$ values on the nature of the ligand substituents prompted us to attempt to use Pickett and Pletcher's²⁰ equation (1) to obtain a new series of ligand parameters, $(dE^\circ/dx)_L$, by solving the equation for this parameter. However, in the course of our investigations, we found several serious drawbacks to the equation. First, we calculated a value for the constant A (based on dichloromethane as solvent and standard calomel electrode as the reference) by comparing the $E_{1/2}$ value found by McCleverty¹ and coworkers for $\text{Cr}(\text{CO})_4^-(\text{CNCH}_3)_2$ (0.59 v) and the values for the $\text{Mn}(\text{CO})_{6-x}(\text{CNCH}_3)_x^+$ complexes found by Treichel²³ and coworkers. In this way a value of $A = 1.50$ was determined. Pickett and Pletcher had obtained values of -0.37 and -0.42 for the ligand parameters of the aryl isocyanides $p\text{-ClC}_6\text{H}_4\text{NC}$ and $p\text{-CH}_3\text{-C}_6\text{H}_4\text{NC}$, respectively. Use of these parameters to obtain

$E_{1/2}$ values for the $\text{Mn}(\text{RNC})_6^+$ complexes in this study produced the values 0.76 v for $[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{PF}_6$ and 0.46 v for $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$ compared to the known values of 1.05 v and 0.93 v, respectively. An examination of the data used by Pickett and Pletcher to obtain their linear relationship reveals the source of the problem. The charge effect term of the equation ($1.48 y$; y = charge on the complex) is incorrect for more highly substituted species. For example, the difference in oxidation potentials of the isostructural pair $\text{Cr}(\text{CO})_6$ and $[\text{Mn}(\text{CO})_6]^+$ is 1.50 volts while the difference for $\text{Cr}(\text{p-ClC}_6\text{H}_4\text{NC})_6^3$ and $[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]^+$ is 0.75 volts, a result of the different σ donor and π acceptor properties of carbonyls vs aryl isocyanides. The flexibility of the carbonyls to accept a greater or lesser portion of the π donation from the metal vs the relatively good σ donor and poor π -acceptor strength of the alkyl isocyanides produces a fairly linear correlation up to the trisubstituted species $\text{Cr}(\text{CO})_3(\text{CNR})_3$ and $[\text{Mn}(\text{CO})_3(\text{CNCH}_3)_3]^+$. However, no such straight line correlation exists for the aryl isocyanide complexes since they have previously shown a range of fluctuating acceptor ability. Thus a series of complexes of the type $\text{Cr}(\text{CO})_{6-x}(\text{RNC})_x$ (R = aryl isocyanide) would be

expected to produce a non-linear plot of number of carbonyls vs $E_{1/2}$ values. The equation, therefore, should be limited to carbonyl complexes of lower substitution $(M(CO)_{6-x}(L)_x)^y$ ($x = 1-3$). Any attempt to apply the relationship to higher substituted species requires the use of a non-linear ligand parameter term and a non-linear charge effect term.

We have shown in this work that a linear relationship does exist between the $E_{1/2}$ values and nature of the ring substituent for a series of $M(RNC)_6$ ($R = \text{aryl isocyanide}$) complexes. It is hoped that theoretical calculations will lead to an even better correlation, perhaps between the shift in LUMO levels and $E_{1/2}$ values due to substituent effect. Several reviews on the electronic effects of substituents attached to benzene rings have been published,⁴⁻⁹ but our work and extended theoretical calculations may make it possible to obtain a better understanding of the meaning of σ parameters.

C. EXPERIMENTAL

All isocyanide complex preparations were carried out under nitrogen. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectral measurements were made on a Beckman IR-10 spectrometer, employing dichloromethane solutions except as noted.

Electrochemical measurements were made using a three-electrode configuration, employing a stationary platinum bead working electrode, platinum spiral counter electrode, and saturated calomel (KCl) reference electrode. Voltage and current functions were controlled using a Princeton Applied Research Electrochemistry System, Model 170, incorporating compensation for internal resistive potential drop. Dichloromethane or acetonitrile were used as solvents with the solution 5×10^{-3} M in substrate. Tetra-butylammonium perchlorate (0.1 M) was employed as the supporting electrolyte.

All of the aryl isocyanides used in this study were prepared by the method of Appel, Kleinstück, and Ziehn,³ by reaction of the appropriate formamide (RNHCHO) with triphenylphosphine, carbon tetrachloride and triethylamine. The liquid ligands were purified by distillation and the

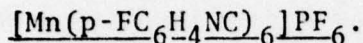
solid ligands by sublimation. Manganese pentacarbonyl bromide, $\text{Mn}(\text{CO})_5\text{Br}$,³ manganese pentacarbonyl chloride, $\text{Mn}(\text{CO})_5\text{Cl}$,³ manganese pentakis (phenyl isocyanide) chloride, $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$,²³ were prepared by previously reported methods. Tetrahydrofuran (THF) was freshly distilled from LiAlH_4 . Absolute ethanol was kept over molecular sieves. All other solvents used during reaction and workup were reagent grade solvents not further purified. Acetonitrile for electrochemical measurements was freshly distilled from P_2O_5 .

Preparation of Known $\text{Mn}(\text{RNC})_6^+$ Complexes.

The complexes $[\text{Mn}(\text{p-CNC}_6\text{H}_4\text{OCH}_3)_6]\text{PF}_6$, $[\text{Mn}(\text{CNC}_6\text{H}_5)_6]\text{PF}_6$, $[\text{Mn}(\text{p-CNC}_6\text{H}_4\text{CH}_3)_6]\text{PF}_6$ and $[\text{Mn}(\text{p-CNC}_6\text{H}_4\text{Cl})_6]\text{PF}_6$ were prepared by the method of Sacco^{4,5} from anhydrous manganese(II) iodide and the appropriate aryl isocyanide followed by metathesis with NH_4PF_6 to form the hexafluorophosphate salt. The complexes were recrystallized from acetone-ether and identified by their characteristic infrared absorptions and melting points.

Preparation of New $\text{Mn}(\text{RNC})_6^+$ Complexes.

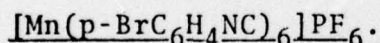
The complexes $[\text{Mn}(\text{RNC})_6]\text{PF}_6$ ($\text{R} = \text{p-NO}_2$, p-NC , p-Br , p-F , m-CF_3 , $-\text{CH}_3$, m-CH_3) were also prepared by the method of Sacco⁴ with slight variations.



To a solution of MnI_2 (anhydrous) (1.5 g, 5.0 mmol) in absolute ethanol (100 ml) was added p- $\text{FC}_6\text{H}_4\text{NC}$ (4.3 g, 35 mmol). The solution was refluxed for 3 h, stirred at room temperature for 12 h, evaporated to dryness, and the residue redissolved in CH_2Cl_2 and filtered. The CH_2Cl_2 solution was then shaken with cold saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$. The organic layer was separated, dried with anhydrous MgSO_4 , and filtered. The solution was again evaporated to dryness and redissolved in hot ethanol- CH_2Cl_2 (90%-10%). An excess of NH_4PF_6 in ethanol was added to precipitate 2.0 g of white flakes in 43% yield (based on MnI_2). The compound darkens and melts at 288-289 °C.

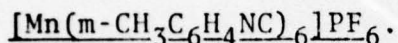
IR: $\nu(\text{CN})$ 2090vs, 2050m(sh) cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}

Data on other compounds prepared in like manner are given below.



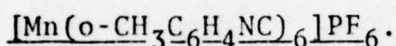
Metathesized in a hot acetone solution of NH_4PF_6 . Evaporation of acetone and recrystallization from CH_2Cl_2 -hexane yielded pale yellow flakes in 20% yield. The compound darkens and melts at 235-236 °C.

IR: $\nu(\text{CN})$ 2090vs cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}



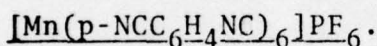
Precipitated as white flakes from ethanol. Recrystallized from CH_2Cl_2 -hexane in 64% yield. The compound darkens and melts at 185-186 °C.

IR: $\nu(\text{CN})$ 2090vs, 2060s(sh) cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}



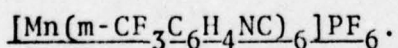
Precipitated as yellow powder from ethanol. Recrystallized as yellow cubes from CH_2Cl_2 -hexane in 47% yield. The compound melts at 230-231 °C.

IR: $\nu(\text{CN})$ 2090vs, 2050m(sh) cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}



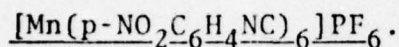
Metathesized in an acetone solution of NH_4PF_6 . Evaporation of acetone and recrystallization from $\text{CH}_3\text{CN-H}_2\text{O}$ yielded yellow cubes in 37% yield. The compound darkens and melts at 258 °C.

IR: $\nu(\text{CN})$ (In CH_3CN) 2090vs, 2045m cm^{-1} ; $\nu(\text{NC})$ 2260w cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}



Reaction refluxed in THF for 24 h. Product precipitated from ethanol solution of NH_4PF_6 . Recrystallized as pale yellow needles from CH_2Cl_2 -hexane in 5% yield. The compound melts at 200 °C.

IR: $\nu(\text{CN})$ 2090vs, 2060s cm^{-1} ; $\nu(\text{PF})$ 840m cm^{-1}

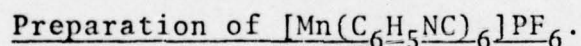


The reaction was refluxed in THF for ~3 h and stirred at room temperature for an additional 12 h. Excess NH_4PF_6 was added to the filtered THF solution and the solution evaporated to dryness. The residue was washed successively with CCl_4 , H_2O , ethanol, and CH_3CN leaving a 27% yield of dark orange product. The compound decomposes without melting at ~300 °C.

IR: $\nu(\text{CN})$ 2090s, 2070m cm^{-1} ; $\nu(\text{PF})$ 840s cm^{-1} (In acetone)

Alternative Methods of Preparation of Hexakis (aryl isocyanide) manganese(I) Complexes

The following example reactions are general and can be applied to any manganese aryl isocyanide system.



A solution of manganese pentakis(phenyl isocyanide) chloride, $\text{Mn(C}_6\text{H}_5\text{NC)}_5\text{Cl}$ (0.60 g, 1.0 mmol) in 50 ml THF was treated with silver hexafluorophosphate, AgPF_6 (0.40 g, 1.5 mmol) producing an immediate precipitate. The reaction was stirred at room temperature for ~12 h, filtered, and the residue washed with CH_2Cl_2 . Addition of hexane precipitated 0.60 g of white needles. The infrared spectrum and cyclic voltammetry were identical with those of the known $[\text{Mn(C}_6\text{H}_5\text{NC)}_6]\text{PF}_6$. The yield without addition of

excess ligand was 88%. Addition of one equivalent of ligand before addition of AgPF_6 improves the yield to near quantitative.

IR: $\nu(\text{CN})$ 2090 vs cm^{-1} ; $\nu(\text{PF})$ 840 cm^{-1}

Anal: Calcd. for $\text{C}_{42}\text{H}_{30}\text{N}_6\text{F}_6\text{PMn}$: C, 61.60; H, 3.68; N, 10.25. Found: C, 61.25; H, 3.78; N, 10.48.

Preparation of $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$.

A solution of manganese pentacarbonyl bromide, $\text{Mn}(\text{CO})_5\text{Br}$ (0.22 g, 0.80 mmol) and $\text{p-NO}_2\text{C}_6\text{H}_4\text{NC}$ (0.65 g, 4.4 mmol) in ~50 ml THF was refluxed for ~48 h. The solution was cooled and 0.35 g (43% yield) $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{Br}$ was recovered as dark orange powder. Low solubility in all common solvents made metathesis difficult, but 0.10 g $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$ was prepared by refluxing an acetone solution of 0.35 g $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{Br}$ and excess NH_4PF_6 for ~1 h, cooling, filtering, and precipitating the product from the acetone solution by addition of hexane. The compound decomposes without melting at ~300 °C. The infrared spectrum was identical to the previously prepared $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]^+$ complex.

The THF solution remaining after removal of $[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_6]\text{Br}$ was evaporated to dryness and the residue redissolved in CH_2Cl_2 . Slow diffusion of diethyl ether into the solution resulted in the crystallization of 0.10 g

of long needles with green reflectances. The complex was found to be $\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5\text{Br}$ and is described in more detail in Chapter VI.

TABLE 1. VOLTAMMETRIC DATA AND SUBSTITUENT PARAMETERS

Complex	$1/2[E_{p,c} + E_{p,a}]^a$	$[E_{p,c}^-]_{p,a}^b$	Process	σ_p^f	σ_I^g	σ_R^h
$[Mn(p-NO_2C_6H_4NC)_6]PF_6^c$	1.31	260	+1 \rightarrow +2	0.778	0.64	0.14
$[Mn(m-CF_3C_6H_4NC)_6]PF_6$	1.14 1.99	80 150	+1 \rightarrow +2 +2 \rightarrow +3	0.415	0.41	0.00
$[Mn(p-BrC_6H_4NC)_6]PF_6$	1.05 1.91	70 140	+1 \rightarrow +2 +2 \rightarrow +3	0.232	0.45	-0.22
$[Mn(p-ClC_6H_4NC)_6]PF_6^d$	1.04 (0.89) ^e 1.90 (1.79) ^e	160 200	+1 \rightarrow +2 +2 \rightarrow +3	0.226	0.47	-0.24
$[Mn(p-FC_6H_4NC)_6]PF_6$	0.99 1.88	175 240	+1 \rightarrow +2 +2 \rightarrow +3	0.062	0.51	-0.45
$[Mn(p-CH_3C_6H_4NC)_6]PF_6^d$	0.93 (0.76) ^e 1.83 (1.69) ^e		+1 \rightarrow +2 +2 \rightarrow +3	-0.170	-0.05	-0.12

TABLE 1. (Contd.)

Complex	$1/2[E_{p,c} + E_{p,a}]^a$	$[E_{p,c} - E_{p,a}]^b$	Process	σ_p^f	σ_I^g	σ_R^h
$[\text{Mn}(\text{m-CH}_3\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$	0.98	200	$+1 \rightarrow +2$	-0.069	-0.08	0.01
	1.92	230	$+2 \rightarrow +3$			
$[\text{Mn}(\text{o-CH}_3\text{C}_6\text{H}_4\text{NC})_6]\text{PF}_6$	1.05	200	$+1 \rightarrow +2$	0.628	0.52	0.11
	2.00	300	$+2 \rightarrow +3$			
$[\text{Mn}(\text{p-NCC}_6\text{H}_4\text{NC})_6]\text{PF}_6$	1.10 ^e	80	$+1 \rightarrow +2$	0.000	0.00	0.00
	1.92 ^e		$+2 \rightarrow +3$			
$[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{PF}_6^d$	1.01		$+1 \rightarrow +2$	0.000	0.00	0.00
	(0.83) ^e		$+2 \rightarrow +3$			
	1.91					
$[\text{Mn}(\text{p-CH}_3\text{OC}_6\text{H}_4\text{NC})_6]\text{PF}_6^d$	(1.77) ^e			-0.268	0.26	-0.53
	0.81		$+1 \rightarrow +2$			
	(0.69) ^e		$+2 \rightarrow +3$			
	1.68					
	(1.55) ^e					

a) Cathodic and anodic peak potentials in volts vs SCE (aq. KCl). Solutions

TABLE 1. (Contd.)

- in CH_2Cl_2 (5×10^{-3} M) with Bu_4NClO_4 (0.1 M) as supporting electrolytes.
- b) Peak separation in mV.
 - c) Low solubility did not allow all of the complex to dissolve; rapid electrode coating required single scan at higher rate.
 - d) Voltammetric data previously reported. Solution in CH_2Cl_2 in ref. 2, solutions in CH_3CN in ref. 3.
 - e) Solutions in CH_3CN (5×10^{-3} M) with Bu_4NClO_4 (0.1 M) as supporting electrolyte.
 - f) Ref. 33.
 - g) Ref. 7.
 - H) $\sigma_R = \sigma_p - \sigma_I$ (difference of the previous two columns).

TABLE 2. $E_{1/2}$ - σ Correlations^a

Parameter	b_1 (volts ⁻¹)	b_0	s	r
σ_I	1.12	-8.62	0.561	0.576
σ_P	2.27	-2.20	0.131	0.975
σ_R	1.15	-1.34	0.402	0.711

a) For regression line $\sigma = b_0 + b_1(E_{1/2})$. $E_{1/2}$ values in CH_2Cl_2 solvent; b_0 = y-intercept; b_1 = slope; s = standard deviation of the slope; r = correlation coefficient.

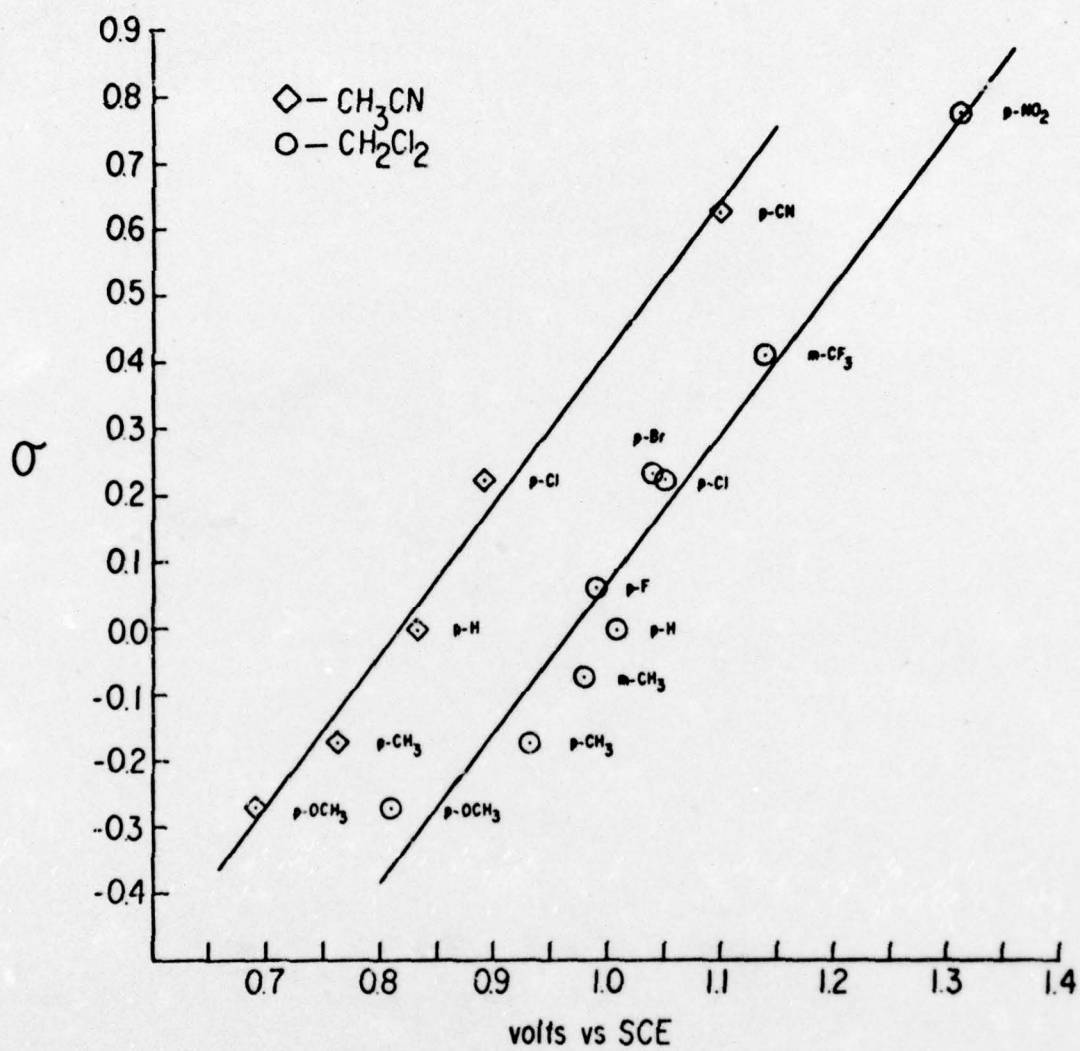
TABLE 3. CALCULATED ENERGY LEVELS FOR p-CNC₆H₄X (eV)^a

X	ring- π^*	π^*	π^* -ring
H	-2.15	5.64	7.06
CH ₃	-1.75	5.78	7.28
OCH ₃	-0.56	6.16	8.32
NO ₂	-5.67	4.81	8.29
Cl	-1.60	5.80	7.43
F	-1.22	5.81	7.73
m-CH ₃	-2.07	5.66	7.24

a) Calculated by the method of ref. 34.

Figure 1

Plot of σ_p vs $E_{1/2}$ for Complexes of the
Type $[\text{Mn}(\text{p-XC}_6\text{H}_4\text{NC})_6]\text{PF}_6$ and $[\text{Mn}(\text{m-XC}_6\text{H}_4\text{NC})_6]\text{PF}_6$



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CHAPTER II
REACTIONS OF ELECTRON - RICH ISOCYANIDE
COMPLEXES OF MANGANESE(I)

A. INTRODUCTION

Previous work in our group on isocyanide complexes of manganese and chromium^{1,2} showed that the ease of oxidation, measured electrochemically as an $E_{1/2}$ value, is substantially dependent on the ligand groups attached to the metal. For example, in the series $[\text{Mn}(\text{CO})_{6-x}(\text{CH}_3\text{NC})_x]^+$ the values of $E_{1/2}$ decreased by about 0.4 v on successive carbonyl substitution by the isocyanide. This result can be equated qualitatively with the net donor characteristics (both σ and π) of the ligand; the effect of substitution of a better donor ligand, CNMe, for a poorer one, CO, is to increase the metal electron density, which in turn causes the metal to be more prone to loss of an electron. Theoretical arguments have added some reassurance to this rationale.³ In attempting to broaden a framework of reference in this area, we prepared various manganese isocyanide complexes of the type $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x\text{X}$, as described in Chapter VI. Our initial interest was directed toward the redox properties of these complexes and to the isolation of products obtainable through one electron oxidation. The electrochemical results suggested that we should attempt to prepare these oxidized species by reaction with AgPF_6 as the oxidizing agent. However, as the work progressed,

it became clear that the oxidation reactions were being superceded by a reaction in which halide extraction was followed by ligand insertion, a not totally unexpected result in view of previous observations by other researchers.⁵

It should be noted here that definite criteria seem to dictate whether isolation of stable $17 e^-$ species is possible.⁶ First, the $18 e^-$ precursor should be reasonably easy to oxidize. This criterion appears to be met in the electron-rich manganese isocyanide complexes. It can also be noted that so far the only $17 e^-$ species which exhibit a stable existence are those that have been formed from easily oxidized precursors. Second, the loss of $1 e^-$ from an $18 e^-$ complex must not seriously weaken the metal ligand bond. This criterion would also appear to be met in the case of the electron rich isocyanide complexes. Finally, the $17 e^-$ complex must resist entering into reactions which will generate another $18 e^-$ species. Dimerization is an obvious example of this. However, this should also not be a problem in the oxidation of the $Mn(CO)_{5-x}^-(RNC)_x$ complexes since it is less likely that a six coordinate metal complex would dimerize. In light of the fact that all of these criteria appear to be met for the $Mn(CO)_{5-x}^-(RNC)_x$ complexes, we expected to isolate a series of $17 e^-$ species. However, as previously mentioned, in

each instance the only reaction occurring was halide ion replacement by an isocyanide ligand. The Ag^+ assisted loss of an X^- ion from these complexes is clearly facile and must occur at a rate greater than the rate of electron transfer. We still believe the oxidized 17 e^- species $[\text{Mn}(\text{CO})_{5-\text{x}}(\text{RNC})_{\text{x}}\text{X}]^+$ can be isolated although a different oxidizing agent (perhaps H_2O_2 or Ce^{+4}) is obviously needed.

Our interest broadened, therefore, to encompass other similar halide extraction and ligand insertion reactions which would reveal the utility and generality of this method. We thus set out to prepare a series of mixed ligand complexes using this new synthetic approach. The new complexes were examined electrochemically to determine the effect of replacing the halide ion with a donor ligand. Also, a series of complexes $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L})]\text{PF}_6$ (L = isocyanide, amines) was prepared to examine the effect on $\nu(\text{CO})$ as L is varied and ultimately to attempt to correlate $\nu(\text{CO})$ with the $E_{1/2}$ of the complex. We also decided to examine the conductivity of a typical $\text{Mn}(\text{RNC})_5\text{X}$ species in a few polar and non-polar solvents to determine what effect, if any, the solvent has on the reaction of this species with AgPF_6 .

B. RESULTS AND DISCUSSION

The results of our electrochemical investigation of complexes of the type $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x\text{X}$ (R = aryl isocyanides; $\text{X} = \text{Cl}, \text{Br}$) indicated that the complexes have $E_{1/2}$ values which allow chemical oxidation of the species by a variety of oxidizing agents. (See Chapter VI).

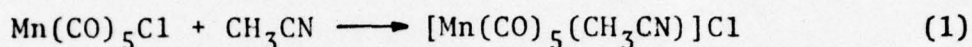
Our initial reaction in this work, therefore, was an attempt to prepare the complex, $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}]\text{PF}_6$, by reaction of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}$ with AgPF_6 in THF. The product isolated turned out to be $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{PF}_6$, indicating that the AgPF_6 is acting as a halide extractor in preference to its anticipated function as oxidizing agent. It should be noted here that previous research in our group by Treichel and Wagner⁹ on the species CpFeL_2X (L = phosphines, phosphites, carbonyl, isocyanide; $\text{Cp} = \text{h}^5\text{-C}_5\text{H}_5$) revealed a similar phenomenon. Thus the attempted oxidations of the species $\text{CpFe}(\text{C}_6\text{H}_5\text{NC})_2\text{I}$ and $\text{CpFe}(\text{CO})(\text{C}_6\text{H}_5\text{NC})\text{I}$ with nitrosyl hexafluorophosphate, NOPF_6 , produced $[\text{CpFe}(\text{C}_6\text{H}_5\text{NC})_3]\text{PF}_6$ and $[\text{CpFe}(\text{CO})(\text{C}_6\text{H}_5\text{NC})_2]\text{PF}_6$, respectively. Interestingly, attempted oxidations of complexes of the type $\text{CpFe}(\text{diphos})\text{X}$ ($\text{X} = \text{CH}_3, \text{Cl}, \text{Sn}(\text{CH}_3)_3, \text{Br}, \text{and I}$; $\text{diphos} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$) with AgPF_6 were successful in forming the $17 e^-$ species, $[\text{CpFe}(\text{diphos})\text{X}]\text{PF}_6$. The chelating effect

of the phosphine ligand probably stabilizes the complex against ligand loss; rate of electron transfer in these reactions must be faster than Ag^+ assisted loss of X^- . In our attempted oxidations of the isocyanide complexes, it is apparent that an intermediate, probably complexed by the solvent, rapidly adds free ligand which is present from the degradation of this same intermediate species in the reaction.

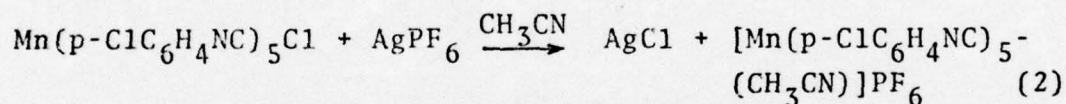
We decided to attempt to determine the role of the solvent in these reactions by examining the conductivity of a representative species, $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$, in solvents of varying polarity and basicity. For comparison, we also measured the conductivities of the known 1:1 electrolytes, Bu_4NBr and $[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{PF}_6$. These data are presented in Table 2. Conductivity measurements of other $\text{Mn}(\text{CO})_5\text{-X}^-$ ($\text{RNC})_x\text{X}$ and $[\text{Mn}(\text{RNC})_6]\text{PF}_6$ species were presented by Treichel¹ and coworkers. An examination of our conductivity data reveals that the conductivity of the MnL_5X complex in CH_2Cl_2 , a non-basic, weakly polar solvent, is definitely higher than a non-electrolyte but only about 10% of the known value for a 1:1 electrolyte.⁷ The conductivity of the complex in THF, a solvent of low polarity but higher basicity, can only be compared to the solubility of Bu_4NBr , since the MnL_6^+ complex is insoluble in THF and no other

published data is available. It is apparent that the solubilities of both Bu_4NBr and $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ in THF are of the same order of magnitude, but in view of the low values it is difficult to reach a conclusion about the significance of the data. The most interesting conductivity data was obtained from the acetonitrile solutions of the test samples. The MnL_6^+ and Bu_4NBr species exhibited conductance values in accordance with published data for 1:1 electrolytes (150-175). The MnL_5X species, however, exhibited a conductance which steadily increased with time and a value less than an order of magnitude different than that obtained for the 1:1 electrolyte. An examination of these conductivity data does allow several points to be made. First, it is apparent that the $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ complex does exhibit a finite conductivity in all solvents tested and a case can be made for the existence of a closely associated ion pair between the metal-ligand fragment and the halide. Second, the conductivity change in CH_3CN might well be complicated by other factors, such as O_2 oxidation. The experimental work in this chapter and the complexes isolated tend to support the ion pair concept. It can be postulated that polar solvents (such as CH_3CN) would accentuate this ion pair producing higher relative conductances.

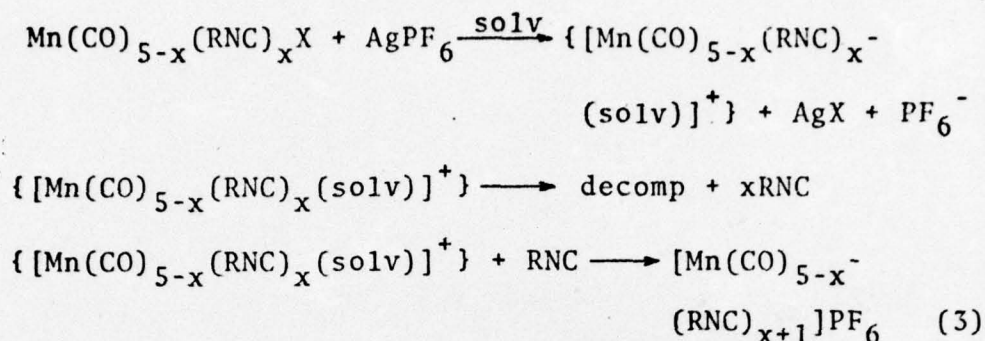
It can be further postulated that a halide displacement reaction of the type previously seen with halocarbonylmanganese complexes⁵



is the predominant mechanism in solutions of haloisocyanidemanganese complexes in strong donor solvents. This could also account for the gradually increasing conductivity of $\text{Mn(p-ClC}_6\text{H}_4\text{NC)}_5\text{Cl}$ in CH_3CN . However, if this mechanism is indeed the dominant one, then the complex $[\text{Mn(p-ClC}_6\text{H}_4\text{NC)}_5(\text{CH}_3\text{CN})]\text{PF}_6$ should be isolable from the reaction



The reaction was attempted as were reactions in other donor solvents (acetone, THF). An immediate yellow precipitate formed and workup of the reaction after ~2 hours at room temperature resulted in the recovery of $[\text{Mn(RNC)}_6]\text{PF}_6$ in high yield (~80%), again indicating the formation and decomposition of some unstable intermediate which supplies ligands to other intermediates to produce the stable product. A more probable mechanism for these halide extraction, ligand insertion reactions can therefore be postulated as follows:



The key to the reaction, therefore, appears to be in the kinetic stability of the intermediate. Thus a stronger donor solvent might be expected to stabilize the intermediate and allow isolation of complexes of the type $[\text{Mn(CO)}_{5-x}(\text{RNC})_x(\text{L})]^+\text{PF}_6^-$.

The complexes $\text{Mn(p-CH}_3\text{C}_6\text{H}_4\text{NC)}_5\text{Cl}$, $\text{Mn(p-CH}_3\text{C}_6\text{H}_4\text{NC)}_4(\text{CO})\text{Cl}$, $\text{Mn(C}_6\text{H}_5\text{NC)}_5\text{Cl}$, and $\text{Mn(C}_6\text{H}_5\text{NC)}_4(\text{CO})\text{Cl}$ were reacted with AgPF_6 in a variety of complexing solvents. The solvents chosen were limited to relatively low boiling liquids to allow easy removal of the solvent under mild conditions before workup of the product.

Reaction of $\text{Mn(C}_6\text{H}_5\text{NC)}_5\text{Cl}$ with AgPF_6 in CH_3NC resulted in the immediate formation of a grayish-white precipitate as was previously noted in the formation of the $[\text{Mn(RNC)}_6]^+\text{PF}_6^-$ complexes from $\text{Mn(RNC)}_5\text{Cl}$ and AgPF_6 in THF. Recovery of the CH_3NC solvent followed by workup of the residue from CHCl_3 -heptane resulted in the recovery of $[\text{Mn(C}_6\text{H}_5\text{NC)}_5]^+\text{PF}_6^-$.

$(\text{CH}_3\text{NC})\text{PF}_6$ in good yield (53%) as the only product. The complex was easily identified by infrared and nmr data (Table 1; Figure 1) as well as accurate elemental analysis.

Reaction of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{Cl}$ with AgPF_6 in pyridine yielded $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{C}_5\text{H}_5\text{N})]\text{PF}_6$; $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with AgPF_6 in CH_3NC , $(\text{CH}_3)_3\text{CNC}$, $\text{C}_5\text{H}_5\text{N}$, and o-toluidine produced $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{CH}_3\text{NC})]\text{PF}_6$, $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{t-BuNC})]\text{PF}_6$, $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{C}_5\text{H}_5\text{N})]\text{PF}_6$, and $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{o-CH}_3\text{C}_6\text{H}_4\text{NH}_2)]\text{PF}_6$ respectively. These complexes were all readily identified from the infrared ($\nu(\text{CN})$, $\nu(\text{CO})$, and $\nu(\text{PF})$ absorptions; Table 1, Figure 1) and nmr data. The nmr data are particularly helpful in identifying the amine complexes, since the characteristic infrared absorptions of the amines used are not observed, probably a function of the low relative abundance of the ligand. Interestingly, reaction of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{X}$ with AgPF_6 in two other amines, triethylamine (NEt_3) and benzylamine ($\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$), failed to produce the expected $[\text{Mn}(\text{RNC})_4(\text{CO})\text{L}]\text{PF}_6$ product. The reaction in NEt_3 produces a clear crystalline complex, as yet unidentified, which exhibits a strong carbonyl absorption, $\nu(\text{CO})$, at 2000 cm^{-1} , a medium isocyanide absorption, $\nu(\text{CN})$, at 2140 cm^{-1} and a $\nu(\text{PF})$ for the PF_6^- salt at 840 cm^{-1} .

The nmr spectrum shows broad unresolved resonances consistent with that of an ethyl group as well as the phenyl and methyl protons of the p-tolyl isocyanide. The elemental analysis of the pure complex, which melts sharply at 165°, is not consistent with that calculated for the $[\text{Mn}(\text{RNC})_4(\text{CO})(\text{NEt}_3)]\text{PF}_6$ complex nor is it consistent with the other possible cationic product, $[\text{Mn}(\text{RNC})_5(\text{CO})]\text{PF}_6$. The reaction in benzyl amine did not yield any isolable product. It is probable that the ability to delocalize the electron density into the ring systems in pyridine and o-toluidine aids in the stabilization of these complexes over the alkyl amine complexes.

The $[\text{Mn}(\text{RNC})_4(\text{CO})(\text{L})]\text{PF}_6$ complexes were readily identifiable by the shift in carbonyl absorption frequency from the neutral $\text{Mn}(\text{RNC})_4(\text{CO})\text{X}$ complex to the cationic product. It was also noted that the isolated complexes could easily be distinguished from the competing reaction product, $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{CO})]\text{PF}_6$, by the frequency of the carbonyl absorption. The complex $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{CO})]\text{PF}_6$ was prepared by reaction of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{X}$ with AgPF_6 in THF and was found to have a carbonyl absorption at 1995 cm^{-1} . The $[\text{Mn}(\text{RNC})_4(\text{CO})(\text{L})]\text{PF}_6$ complexes all exhibit carbonyl absorptions at lower frequencies and a definite

correlation of $\nu(\text{CO})$ with the π -acceptor strength of L is noted. These spectra are shown in Figure 1. This correlation can be rationalized as follows. When L is a poor π -acceptor (pyridine, o-toluidine), the remaining ligands must accept a larger share of the π donation from the electron-rich metal. It has previously been shown^{5,10} that carbonyl ligands are better π -acceptors and exhibit a greater flexibility in π -bonding to the metal than isocyanides (See Chapters I, IV, VI). Thus it is not surprising that the single carbonyls in these complexes reflect the variable π -donation from the metal more than the isocyanides. Furthermore, the invariance of $\nu(\text{CN})$ to the changes in extent of metal π -donation has been discussed in depth in Chapter I and it is presumed that the lowest unoccupied molecular orbital (LUMO) on the aryl isocyanide is again primarily localized on the ring instead of the CN antibonding orbital.

To examine this correlation of $\nu(\text{CO})$ with π -acceptor strength of the ligands, electrochemical measurements of these complexes were also made. These data are presented in Table 3. The current-potential curves for the $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L})]\text{PF}_6$ complexes all exhibit a well-behaved one-electron reversible system based on the absolute

values of the anodic and cathodic peak currents. The curves again do not meet the requirements for electrochemical reversibility ($|E_{p,c} - E_{p,a}| < 0.059 \text{ v}$) although the separations can be manipulated by varying the scan rate without affecting the relative intensities of anodic and cathodic currents. The systems therefore are probably chemically reversible, but electrochemically affected by the variations in properties of measuring hardware, as previously discussed in Chapter I.

An examination of the electrochemical data does reveal a consistent range of $E_{1/2}$ values; the existence of a correlation with the type of ligand and in turn the $\nu(\text{CO})$ values is apparent. It is worthwhile to note the large shift in $\nu(\text{CO})$ values (1995 cm^{-1} for $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5^-(\text{CO})]\text{PF}_6$; 1935 cm^{-1} for $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})(\text{CO})(\text{o-toluidine})]\text{PF}_6$) compared to the relatively small range of $E_{1/2}$ values (1.21 to 1.04 v), a probable function of the π -accepting flexibility of the carbonyl. These data are plotted in Figure 2. A least-squares fitting of the data¹¹ reveals that an excellent correlation between $\nu(\text{CO})$ and $E_{1/2}$ does exist. The regression line, $E_{1/2} = b_0 + b_1(\nu(\text{CO}))$, has y-intercept $b_0 = -4.00 \text{ v}$, slope $b_1 = 0.00261 \text{ v-cm}^{-1}$, standard deviation of the slope $s = 0.000180$, and a correlation coefficient $r = 0.991$. This correlation is not

unexpected in view of the research of other investigators and our own research in Chapter I. McCleverty¹⁰ and co-workers had previously noted correlations of $E_{1/2}$ with the A_1 carbonyl absorption mode of complexes of the type $M(\text{CO})_{6-n}(\text{RNC})_n$ ($M = \text{Cr, Mo, W}$; $n = 1-3$; $R = \text{alkyl or aryl groups}$). Also, Fenske³ and Sarapu noted a similar correlation of carbonyl force constants, $k(\text{CO})$, and stretching frequencies, $\nu(\text{CO})$, with $E_{1/2}$ values for the complexes $\text{Mn}(\text{CO})_{5-x}(\text{CH}_3\text{NC})_x\text{Br}$ ($x = 0-4$) and $\text{Mn}(\text{CO})_{6-x}(\text{CH}_3\text{NC})_x^+$ ($x = 1-6$). We attempted to prepare other $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L})]\text{PF}_6$ complexes and measure their $E_{1/2}$ values to obtain more points for the correlation plot. This, similar reactions of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{X}$ with AgPF_6 in the presence of large excesses of $\text{As}(\text{p-tolyl})_3$, $\text{P}(\text{p-tolyl})_3$, and $\text{P}(\text{C}_6\text{H}_5)_3$ were attempted. In each case it appeared that probable complex formation of the phosphines and arsines with the AgPF_6 prevented the halide extraction process and the expected products were not obtained.

The electrochemical measurements of the complexes $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{C}_5\text{H}_5\text{N})]\text{PF}_6$ and $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CH}_3\text{NC})]\text{PF}_6$ also deserve special mention.

The $E_{1/2}$ value for the complex $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CH}_3\text{NC})]\text{PF}_6$ (0.93 v), when compared to the value for the complex $[\text{Mn}-$

$(C_6H_5NC)_6]PF_6$ (1.01 v; see Chapter I), presents further evidence of the significantly poorer π -acceptor ability of alkyl vs aryl isocyanides. Likewise, the $E_{1/2}$ value of the complex $[Mn(p-CH_3C_6H_4NC)_5(C_5H_5N)]PF_6$ (0.62 v), when compared to that of the complex $[Mn(p-CH_3C_6H_4NC)_6]PF_6$ (0.93 v; Chapter I), shows the even poorer π -acceptor ability of the pyridine ligand. Of added interest, a comparison of $E_{1/2}$ differences between the complexes $[Mn(p-CH_3C_6H_4NC)_4-(CO)(pyr)]PF_6$ and $[Mn(p-CH_3C_6H_4NC)_5(CO)]PF_6$ (0.12 v) and the complexes $[Mn(p-CH_3C_6H_4NC)_5(pyr)]PF_6$ and $[Mn(p-CH_3C_6H_4NC)_6]PF_6$ (0.31 v) presents an insight into π -acceptor flexibility of the carbonyl.

We have presented a synthetic method which was found to be applicable to $Mn(CO)_{5-x}(RNC)_xX$ complexes in general and it is conceivable that variations of x and R would allow the formation of complexes of the type $[Mn(CO)_{5-x}-(RNC)_x(L)]PF_6$ with even weaker π -ligands. It is also conceivable that this technique might stimulate further investigations into the formation of complexes which would coordinate ligands at lower metal oxidation state and release or exchange the ligand when oxidized.

C. EXPERIMENTAL

All reactions were run under a nitrogen atmosphere. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-10, using dichloromethane solutions. Nuclear magnetic resonance spectra were taken on a JEOL MH-100 100 MHz instrument. Conductivity measurements were determined at 26 °C using a Beckman conductivity bridge, Model RC-18A, and a Beckman conductivity cell with cell constant $k = 0.20$, employing dry THF and acetonitrile as solvents.

Electrochemical measurements were made as described in the Experimental section of Chapter I.

All isocyanides were prepared as described in Chapter I. Manganese pentakis (p-chlorophenyl isocyanide) chloride, $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$, manganese tetrakis (p-tolyl isocyanide) carbonyl halide, $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$), were prepared as described in Chapter VI. Manganese pentakis (phenyl isocyanide) chloride, $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$, and manganese tetrakis (phenyl isocyanide) carbonyl halide, $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$), were prepared by the method of Treichel, Dirreen, and Mueh.¹

All other chemicals and solvents were used as purchased without further purification.

Attempted Preparation of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}]\text{PF}_6$ -

Preparation of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{PF}_6$.

To a solution of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}$ (0.65 g, 1.0 mmol) in 100 ml THF was added AgPF_6 (0.40 g; 1.5 mmol). The solution was stirred at rt for ~2 h, evaporated, and the residue washed with CH_2Cl_2 . Addition of hexane to the CH_2Cl_2 solution precipitated 0.60 g of white needles. The compound has the same melting point (264 °C) and infrared spectrum as the known complex, $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{PF}_6$.

Anal. Calcd. for $\text{C}_{42}\text{H}_{30}\text{N}_6\text{PF}_6\text{Mn}$: C, 61.6; H, 3.68; N, 10.25.

Found: C, 61.25; H, 3.78; N, 10.48.

Preparation of $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{CO})]\text{PF}_6$.

To a solution of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Br}$ (0.25 g, 0.42 mmol) in 30 ml THF was added a solution of AgPF_6 (0.15 g, 0.60 mmol) and $\text{p-CH}_3\text{C}_6\text{H}_4\text{NC}$ (0.10 ml) in 20 ml THF. The solution was stirred at rt for ~2 h, evaporated, and the residue washed with CH_2Cl_2 . The CH_2Cl_2 was removed and 0.25 g of product was precipitated from acetone-ether in 77% yield. The compound melts at 85-86 °C.

Anal. Calcd. for $\text{C}_{41}\text{H}_{35}\text{N}_5\text{OPF}_6\text{Mn}$: C, 60.52; H, 4.34; N, 8.61.

Found: C, 60.77; H, 4.60; N, 7.93.

Preparation of $[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{PF}_6$.

To a solution of $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ (0.40 g, 0.51 mmol) in 50 ml acetone was added AgPF_6 (0.25 g, 1.0 mmol) and the reaction was stirred for 1 h. The solution was filtered and the acetone removed. The residue was redissolved in CHCl_3 and pale yellow crystals (0.15 g) were precipitated with hexane in 34% yield. The infrared spectrum, melting point, and cyclic voltammetry data are identical with those of the known $[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{PF}_6$.

Preparation of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CH}_3\text{NC})]\text{PF}_6$.

To a suspension of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ (0.60 g, 1.0 mmol) in 25 ml CH_3NC was added AgPF_6 (0.30 g, 1.2 mmol). The mixture was heated to 50 °C for 2 h to dissolve the reactants, then stirred at rt for 16 h. The CH_3NC was distilled off and collected. The residue was washed with CHCl_3 and 0.40 g of white cubes precipitated by addition of heptane in 53% yield. The compound melts at 172-174 °C.

Anal. Calcd. for $\text{C}_{37}\text{H}_{28}\text{N}_6\text{F}_6\text{PMn}$: C, 58.80; H, 3.70; N, 11.10.

Found: C, 58.81; H, 3.60; N, 10.50.

Preparation of $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{C}_5\text{H}_5\text{N})]\text{PF}_6$.

To a solution of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{Cl}$ (0.40 g, 0.60 mmol) in 25 ml pyridine was added AgPF_6 (0.25 g, 1.0 mmol). The reaction was stirred at rt for 1 h, the pyridine was

removed, and the residue was washed with CH_2Cl_2 . The CH_2Cl_2 was removed and 0.13 g of yellow cubes were crystallized from acetone/ether in 25% yield. The compound melts at 183-185 °C.

Anal. Calcd. for $\text{C}_{45}\text{H}_{40}\text{N}_6\text{F}_6\text{PMn}$: C, 62.50; H, 4.66; N, 9.72.

Found: C, 63.32; H, 5.65; N, 8.90. (Analysis slightly off due to contamination with Bu_4NClO_4 from electrochemical studies).

Preparation of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CO})]\text{PF}_6$.

To a solution of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Br}$ (0.58 g, 1.0 mmol) in 100 ml THF was added AgPF_6 (0.40 g, 1.5 mmol). Reaction stirred at rt for 2 h. The solvent was removed and the residue washed with CHCl_3 . Addition of heptane gave 0.30 g of pale yellow cubes in 51% yield. The infrared spectrum and cyclic voltammetry data are identical to that of the known $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CO})]\text{PF}_6$.

Preparation of $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{CH}_3\text{NC})]\text{PF}_6$.

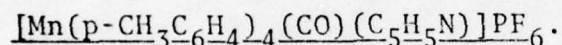
To a solution of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ (0.30 g, 0.50 mmol) in 25 ml CH_3NC was added AgPF_6 (0.15 g, 0.60 mmol). The reaction was refluxed for 12 h, the CH_3NC was removed, and the residue washed with CH_2Cl_2 . Addition of heptane to the filtrate resulted in the precipitation of 0.20 g of white cubes of $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{CH}_3\text{NC})]\text{PF}_6$.

PF₆ in 54% yield. The compound melts at 201-203 °C.

Anal Calcd. for C₃₅H₃₁N₅OF₆PMn: C, 56.99; H, 4.23; N, 9.50.

Found: C, 57.02; H, 4.07; N, 9.60.

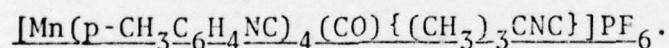
The following compounds were prepared analogously by reaction of Mn(p-CH₃C₆H₄NC)₄(CO)X (X = Cl, Br) with AgPF₆ in various complexing solvents.



Obtained as yellow crystals from CH₂Cl₂-hexane in 77% yield after reacting in pyridine for 24 h at rt. The compound melts at 174-176 °C.

Anal. Calcd. for C₃₈H₃₃N₅OF₆PMn: C, 58.80; H, 4.29; N, 9.03.

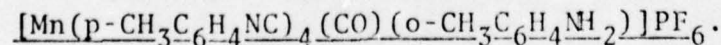
Found: C, 58.87; H, 4.25; N, 8.85.



Obtained as clear rectangles from CH₂Cl₂-hexane in 80% yield after reacting in (CH₃)₃CNC at 50 °C for 24 h. The compound melts at 182-184 °C.

Anal. Calcd. for C₃₈H₃₇N₅OF₆PMn: C, 58.54; H, 4.78; N, 8.98.

Found: C, 58.40; H, 4.77; N, 8.85.



Obtained as yellow needles from CH₂Cl₂-hexane in 71%

yield after reacting in o-toluidine at 50 °C for 24 h. The compound melts at 150 °C.

Anal. Calcd. for $C_{40}H_{37}N_5OF_6PMn$: C, 59.78; H, 4.64; N, 8.72.

Found: C, 59.84; H, 4.73; N, 8.68.

TABLE 1. INFRARED AND PROTON MAGNETIC RESONANCE DATA

Compound	IR Spectral Data (cm^{-1}) ^a			NMR	
	C≡N	C=O	Other	τ	(intensity) ^b
$[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5(\text{CO})]\text{PF}_6$	2200vw, 2090vs	1995s	845[ν_{PF}]		
$[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO}) - (\text{t-BuNC})]\text{PF}_6$	2140w, 2100vs	1985m(br)	845m[ν_{PF}]	2.80s(15) 7.64s(12) 8.44s(9)	
$[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO}) - (\text{CH}_3\text{NC})]\text{PF}_6$	2160w, 2100vs	1980s	845s[ν_{PF}]	2.76m(16) 6.40s(3) 7.64s(12)	
$[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO}) - (\text{C}_5\text{NH}_5)]\text{PF}_6$	2090vs	1945m(br)	845s[ν_{PF}]	1.24d(2) 2.24, 2.56(3) 2.76m(16) 7.64s(12)	
$[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO}) - (\text{o-CH}_3\text{C}_6\text{H}_4\text{NH}_2)]\text{PF}_6$	2090s	1935w(br)	845m[ν_{PF}]	2.80s(b) (20) 3.08s, o(b) 5.72a(2) ^b 7.64s(15)	

TABLE 1. (Contd.)

Compound	IR Spectral Data (cm^{-1}) ^a			τ (intensity) ^b
	C \equiv N	C=O	Other	
[Mn(p-CH ₃ C ₆ H ₄ NC) ₅ (C ₅ NH ₅)PF ₆]	2100m(sh), 2075s, 2040m		845m[ν_{PF}]	1.15d(2) 2.24, 2.56m(3) 2.68s(16), 2.84s(4) 7.62s(15)
[Mn(C ₆ H ₅ NC) ₅ (CH ₃ NC)]PF ₆	2200vw, 2140w 2070vs		845s[ν_{PF}]	2.60s(25) 6.44s(3)
[Mn(C ₆ H ₅ NC) ₅ (CO)]PF ₆	2190vw, 2100vs	1990m	845s[ν_{PF}]	
[Mn(C ₆ H ₅ NC) ₆]PF ₆	2090vs		845s[ν_{PF}]	
[Mn(p-ClC ₆ H ₄ NC) ₆]PF ₆	2090s		845s[ν_{PF}]	

a) Low resolution data, Beckman IR-10, using CH₂Cl₂ solutions.

b) CDCl₃ used as solvent; tetramethylsilane internal standard $\tau=10$; b=broad, o=overlapping; s=singlet, d=doublet, m=multiplet.

TABLE 2. CONDUCTIVITY DATA

Compound	$(\text{cm}^2 \cdot \text{mol}^{-1} \cdot \text{ohm}^{-1})$		
	CH_2Cl_2^a	THF^b	CH_3CN^c
CH_2Cl_2	8×10^{-6}		
THF		3×10^{-6}	
CH_3CN			16×10^{-6}
Bu_4NBr	50	2	175
$[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{PF}_6$	52		134
$\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$	6	0.5	27 - initial 30 - after 5 min. 33 - after 10 min.

- a) CH_2Cl_2 solution (approx. 5×10^{-4} M). Value reported⁷ for a 1/1 electrolyte in CH_2Cl_2 is 78.
- b) THF solution (approx. 5×10^{-4} M).
- c) CH_3CN solution (approx. 5×10^{-4} M). Value reported⁸ for a 1/1 electrolyte in CH_3CN is 135-155.

TABLE 3. VOLTAMMETRIC DATA

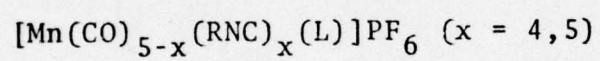
Compound	$1/2[E_{p,c} + E_{p,a}]^a$	$ E_{p,c} - E_{p,a} ^b$
$[Mn(p-CH_3C_6H_4NC)_5(CO)]PF_6$	1.21	200 mV
$[Mn(p-CH_3C_6H_4NC)_4(CO) - (t-BuNC)]PF_6$	1.18	210 mV
$[Mn(p-CH_3C_6H_4NC)_4(CO) - (CH_3NC)]PF_6$	1.16	220 mV
$[Mn(p-CH_3C_6H_4NC)_4(CO) - (C_5NH_5)]PF_6$	1.09	280 mV
$[Mn(p-CH_3C_6H_4NC)_4(CO) - (o-CH_3C_6H_4NH_2)]PF_6$	1.04	260 mV
$[Mn(C_6H_5NC)_5(CH_3NC)]PF_6$	0.93	170 mV
$[Mn(p-CH_3C_6H_4NC)_5(C_5NH_5)]PF_6$	0.62	200 mV

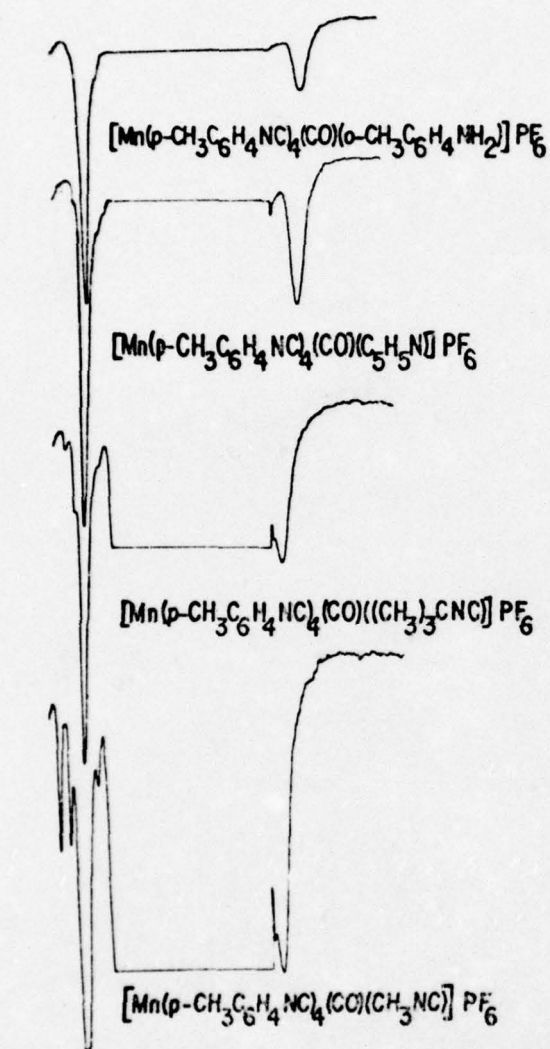
a) Cathodic and anodic peak potentials in volts vs saturated calomel electrode (aq. KCl). Solutions in CH_2Cl_2 (5×10^{-3} M) with $[Et_4N][ClO_4]$ (0.1 M) as base electrolyte. All potentials for the process $+1 \rightarrow +2$.

b) Although the peak separations do not meet the required 0.06 v needed for one-electron reversible systems, the peaks do appear well-behaved and the separations can be manipulated by varying the scan rates.

Figure 1

Infrared Spectra of Complexes of the Type





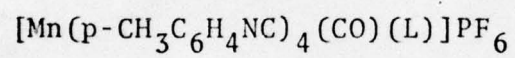
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(CM^{-1})

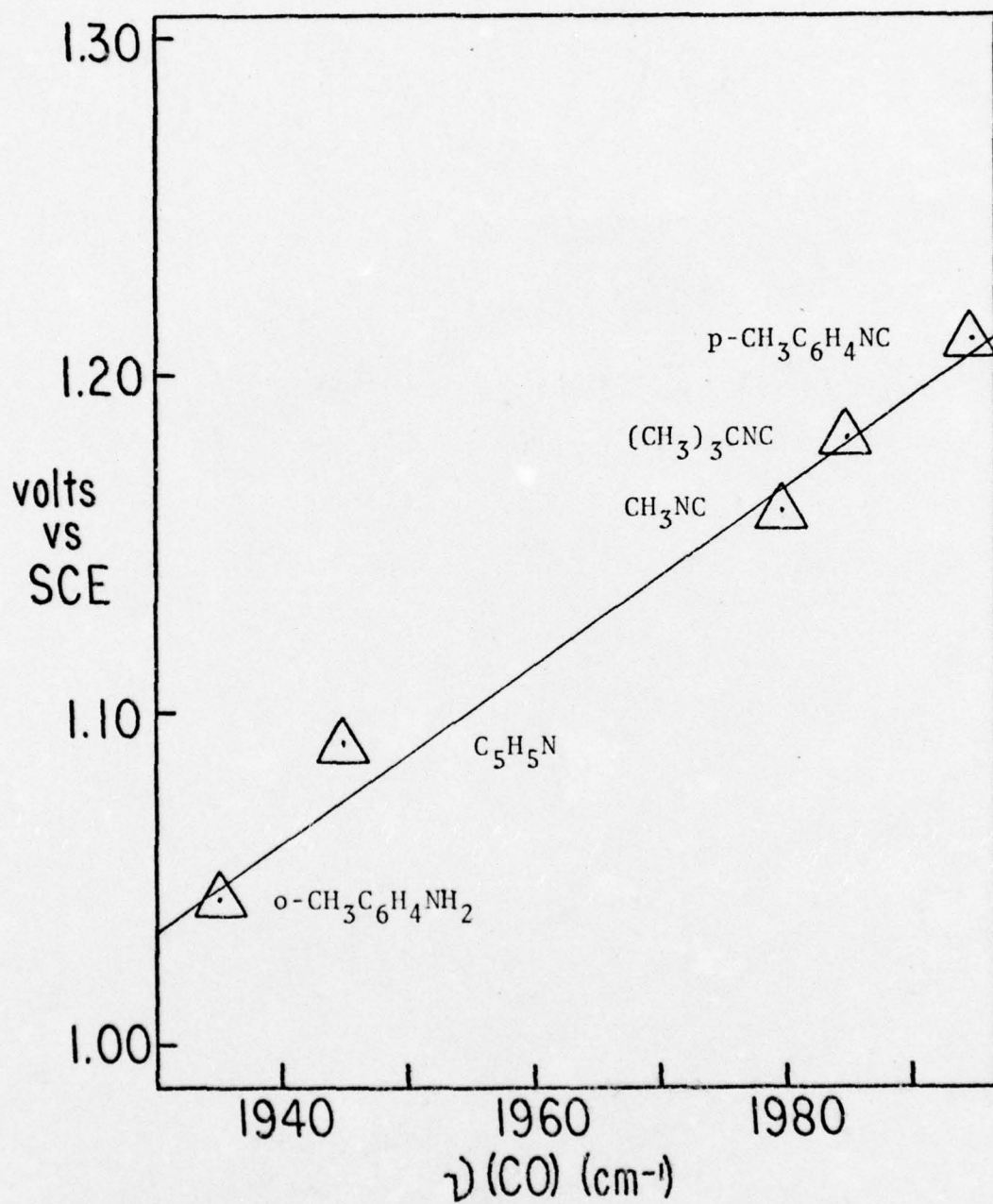


2300 2000 1600
(CM^{-1})

Figure 2

Plot of $\nu(\text{CO})$ vs $E_{1/2}$ for the Complexes





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10. J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd and J. A. McCleverty, J. Chem. Soc., Dalton, 1246 (1972).
11. We are again indebted to Lance Byers of the research group of Dr. L. F. Dahl for his assistance and the use of his least-squares program for the Hewlett-Packard 9820-A calculator.

CHAPTER III

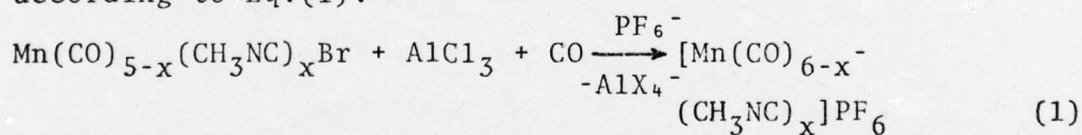
SPECIFIC SYNTHESIS AND ELECTROCHEMISTRY OF
ISOMERIC $[\text{Mn}(\text{CO})_{6-n}(\text{CH}_3\text{NC})_n]^+$ ($n=3,4$) COMPLEXES

SPECIFIC SYNTHESIS AND ELECTROCHEMISTRY OF
ISOMERIC $[\text{Mn}(\text{CO})_{6-n}(\text{CH}_3\text{NC})_n]^+$ ($n=3,4$) COMPLEXES

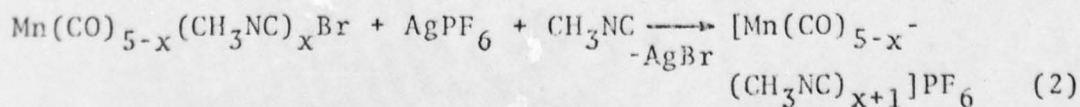
A. INTRODUCTION

The reaction of AgPF_6 with a variety of $\text{MnL}_n(\text{CO})_{5-n}^X$ complexes resulting in halide extraction and ligand insertion, as discussed in Chapter II, was found to be generally applicable to a wide variety of reactions. The reactions of the complexes $\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_3\text{Br}$ and $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2\text{Br}$ with AgPF_6 proved to be particularly interesting.

Earlier research by Treichel and Dirreen¹ had resulted in the synthesis of complexes $[\text{Mn}(\text{CO})_{6-x}(\text{CH}_3\text{NC})_x]^+$ ($x=1-4$), according to Eq.(1).

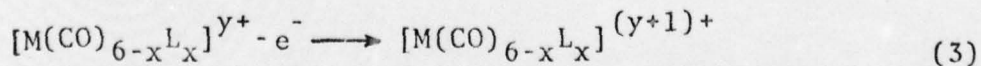


The synthesis of cationic metal carbonyls from metal carbonyl halides, halide acceptor, and ligand is well documented³ and has been applied to the synthesis of a variety of different complexes. The reaction cannot be used, however, when the ligand is an isocyanide and the halide acceptor is AlCl_3 since AlCl_3 causes rapid polymerization of the ligand. The use of AgPF_6 as the halide acceptor therefore led to the reactions described by Eq.(2).



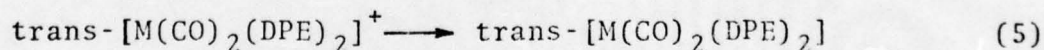
Interestingly, this reaction yielded complexes which were isomers of the products described in the earlier study. Thus fac- $\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_2\text{Br}$ yielded fac- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_3]\text{PF}_6^2$ and $\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_3\text{Br}$, a mer isomer with cis carbonyls, gave cis- $[\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_4]\text{PF}_6$; the respective mer- and trans-isomers had been obtained in the carbonylation reactions from $\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_3\text{Br}$ and $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$, respectively. This represents the only known example of specific synthetic preparation of isomeric complexes of the type $[\text{M}(\text{CO})_{6-x}\text{L}_x]^{y+}$.

Earlier research indicated¹ that the ease of oxidation of the $[\text{Mn}(\text{CO})_{6-n}(\text{CH}_3\text{NC})_n]\text{PF}_6$ complexes, measured as $E_{1/2}$ values in a cyclic voltammetry experiment, was dependent on the extent of isocyanide substitution. Thus the $E_{1/2}$ value for $[\text{Mn}(\text{CH}_3\text{NC})_6]\text{PF}_6$ in CH_3CN vs SCE was +0.38 v, and sequential replacement of CH_3NC by CO raised this value by about 0.5 v per isocyanide. These data could be rationalized by consideration of the ligand donor and acceptor properties and were supported by a good linear correlation of $E_{1/2}$ values with calculated HOMO energies.⁴ Pickett and Pletcher⁶ have noted that electrode potentials for the oxidation of a series of metal carbonyl species



measured in the same inert solvent and versus the same reference electrode should be a measure of the relative HOMO energies if the energies of the MO's are unperturbed by

removal of the electron from the HOMO and if the change in free energy of solvation during the oxidation is approximately constant throughout the series. These restrictions are usually met in practice. Other researchers^{4,12} have correlated changes in $\nu(\text{CO})$ with $E_{1/2}$ values in complexes of the type $[\text{Mn}(\text{CO})_{6-x}\text{L}_x]$. As x increases, the A_1 $\nu(\text{CO})$ stretching frequency decreases when L is a less effective π -acceptor than CO . This correlation is further supported by the plot of $\nu(\text{CO})$ vs $E_{1/2}$ for the complexes $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L})]\text{PF}_6$ presented in Chapter II. A recent paper⁵ noted a difference in $E_{1/2}$ values between the complexes cis- and trans- $\text{M}(\text{CO})_2(\text{DPE})_2$ ($\text{DPE}=1,2$ -bis(diphenylphosphino)ethane $\text{M} = \text{Cr}, \text{Mo}, \text{W}$) and rationalized the difference on the basis of preferential π -bonding to the carbonyls. The authors determined a general series of electrode processes for all of the metal complexes.

$$\text{cis-}[\text{M}(\text{CO})_2(\text{DPE})_2] \xrightleftharpoons{e} \text{cis-}[\text{M}(\text{CO})_2(\text{DPE})_2]^+ \xrightarrow{\text{fast}} \text{trans-}[\text{M}(\text{CO})_2(\text{DPE})_2]^+ \quad (4)$$


Although the electrochemical data revealed evidence for the existence of a variety of isomeric forms, it must be noted that only one isomer is stable in a given oxidation state, a phenomenon previously reported by others.⁹ The manganese isomers, therefore, provide a rare if not unique example of stable isomers of this type in the same oxidation state. Consequently, electrochemical investigations and molecular

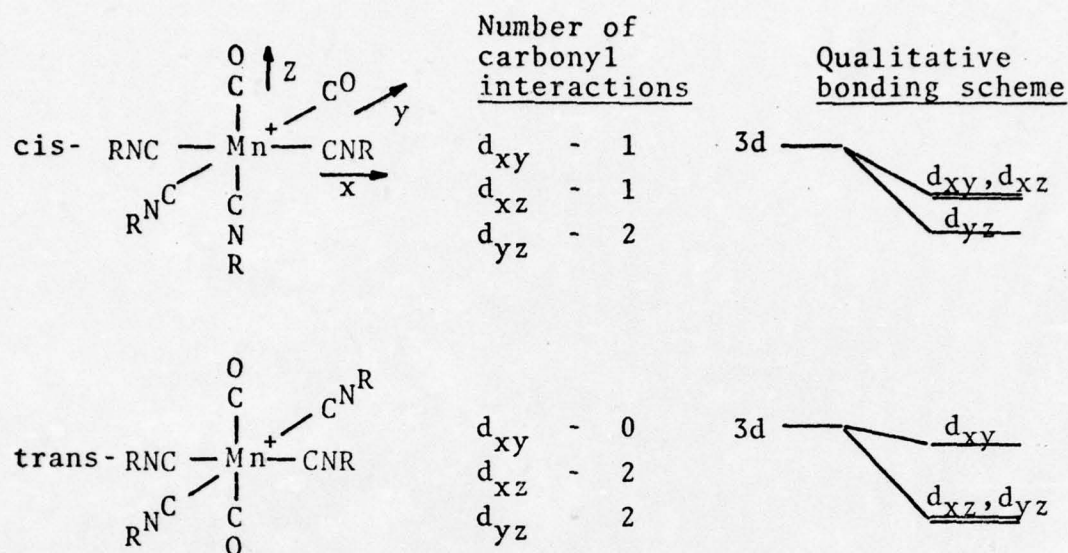
orbital calculations on the new isomers were initiated to obtain quantitative substantiation for the qualitative picture.

B. RESULTS AND DISCUSSION

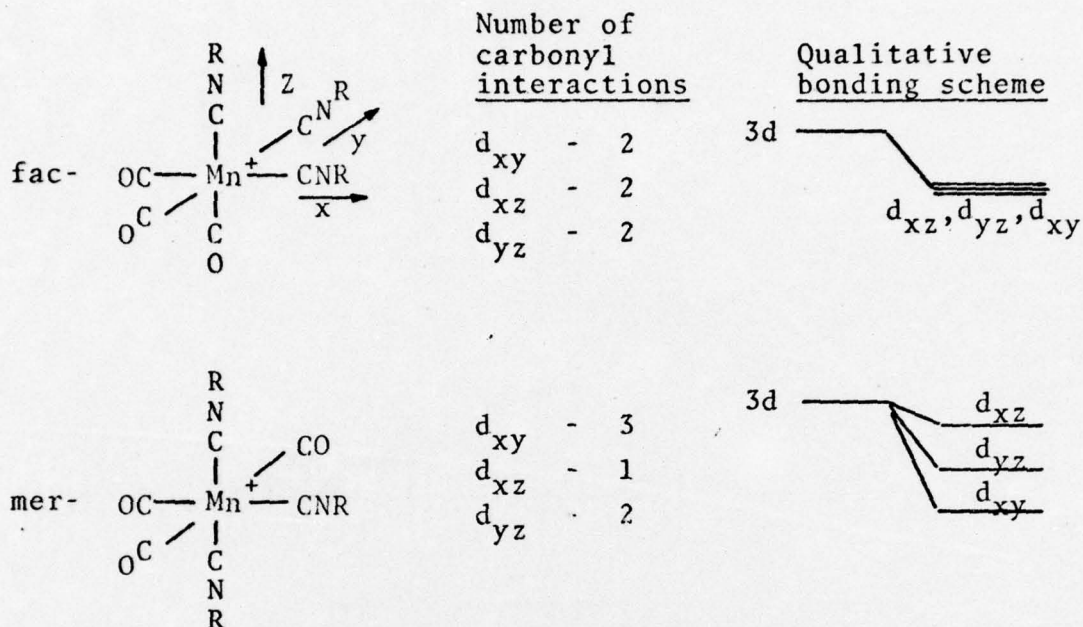
Synthetically, the reactions producing fac- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_3]\text{PF}_6$ and cis- $[\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_4]\text{PF}_6$ were remarkably straight-forward and gave high yields of single products. The isomeric species were readily identified using infrared spectroscopy by observing $\nu(\text{CO})$ and $\nu(\text{CN})$ vibrational frequencies, which are sharp and well-defined (Fig. 1). The specificity of the reactions, in which the ligand assumed the coordination position occupied by the halide ion, is consistent with the AgPF_6 reactions previously reported (Chapter II). Surprisingly, although the general nature of this type of halide extraction and ligand insertion reaction is well known,³ no effort has been directed toward determining the stereochemistry of these reactions, few mechanisms have been offered, and no mechanism has been substantiated. Yet it is apparent that in the systems studied here the incoming ligand assumed the specific coordination position occupied by the halide ion. The retention of stereochemistry seems to argue against a simple dissociative mechanism since a five-coordinate intermediate would most likely be capable of intramolecular ligand exchange. The low polarity of the solvent, THF, probably precludes full dissociation of the halide anion, and a closely associated ion pair might be postulated to precede ligand attack and halide displacement. Support for this

ion pair concept was presented in Chapter II, where measurements on the conductivity of $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ in different solvents showed a range of conductances consistent with a partially dissociated species.

The $E_{1/2}$ values measured for the isomeric cis- and trans- $[\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_4]\text{PF}_6$ and mer- and fac- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_3]\text{PF}_6$ complexes differ by about 0.2v (Table 2, Figure 2) per isomer set. This difference can be rationalized qualitatively, as was previously done for cis- and trans- $\text{M}(\text{CO})_2(\text{DPE})_2$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) isomers,⁵ and furthermore can now be substantiated quantitatively from the molecular orbital calculations.¹³ Qualitatively, two postulates must be made to develop a clear picture of the ligand to metal interactions. First, within isomers of $\text{Mn}(\text{CO})_{6-n}(\text{L})_n^+$, the levels of the primarily metal π -bonding orbitals (the t_{2g} set in idealized O_h symmetry) will be primarily a function of the ligand environment, i.e., the number of carbonyl interactions vs the methyl isocyanide interactions available. Second, it is assumed that a carbonyl group is more stabilizing in π -bonding than a methyl isocyanide group. The first postulate allows the assumption that the d orbitals for each isomer will have the same energy before bonding. Thus, for cis- and trans- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$, the following bonding picture can be formulated:



This formulation predicts a HOMO for the cis-isomer which is a mixture of d_{xz} and d_{xy} while the trans-isomer HOMO should be mainly composed of d_{xy} and higher in energy than the cis-form, with no CO interaction at all. This is confirmed by the quantitative calculations which show a HOMO energy for the trans-isomer of -10.19ev, compared with -10.62ev for the cis-species (Table 2). Also, the trans-complex HOMO orbital was found to be 74.5% $3d_{xy}$ and 23.6% $\text{CH}_3\text{NC } 3e (\pi^*)$ in character. In the cis-isomer, HOMO was found to be a composite of metal (35.2% d_{xy} , 34.8% d_{xz}), carbonyl 2π (10.8%), cis isocyanide $3e$ (11.5%) and trans isocyanide $3e$ (5.5%). The same type of interaction picture can be drawn for the fac- and mer- $[\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_3]\text{PF}_6$:



This formulation predicts that the top three MO's in the fac-isomer should be degenerate and the character of the HOMO should thus be a composite of d_{xz} , d_{yz} , and d_{xy} . The mer-isomer should have the higher HOMO and be easier to oxidize. This is again confirmed by the quantitative calculations. The top three MO's in the fac-isomer were found to have energies of -11.86ev, -11.87ev, and -11.87ev. The HOMO of the mer-isomer was found to have an energy level of -11.45ev while the energy of the first level below the HOMO, predicted qualitatively to have the same energy as the HOMO of the fac-isomer, was calculated to have an eigenvalue of -11.82ev. A plot of the $E_{1/2}$ values vs the HOMO's for the new isomers shows that they do indeed fit the straight line correlation previously determined by Fenske and Sarapu⁴ for the other

$\text{Mn}(\text{CO})_{6-n}(\text{CH}_3\text{NC})_n^+$ complexes (Figure 3). Application of this qualitative explanation for the variance in $E_{1/2}$ values to the only remaining isomer set in this series, cis- and trans- $[\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_4]\text{PF}_6$, leads to some interesting conclusions. Using the same type of qualitative scheme as that applied previously to the $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$ and $[\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_3]\text{PF}_6$ isomers, and using the same coordinate system as for cis- and trans- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$ with CH_3NC and CO interchanged, it can be shown that the HOMO energies of the $[\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_4]\text{PF}_6$ isomers should be the same, the character of the cis-isomer HOMO consisting mainly of d_{yz} while the character of the trans-isomer HOMO should be mixture of d_{xz} and d_{yz} . Therefore, the trans-isomer would be expected to have the same $E_{1/2}$ value as the cis-species, +2.14 volts vs SCE in CH_3CN . Unfortunately, the complex, trans- $[\text{Mn}(\text{CO})_4(\text{CH}_3\text{NC})_2]\text{PF}_6$, has thus far been synthetically elusive. Halide extraction and ligand insertion reactions of the complexes $\text{Mn}(\text{CH}_3\text{NC})(\text{CO})_4\text{Br}$ and $\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_3\text{Br}$ with CH_3NC and CO respectively in both cases give cis- $[\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_4]\text{PF}_6$. The most promising approach to the synthesis of this species may be a photochemical reaction, although several attempts to date have been unsuccessful. Interestingly, photolysis of a solution of cis- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$ for a short period of time (~ 1 h) led to the formation of trans- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$ in $\sim 35\%$ yield while photolysis of a solution of cis-

$[\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})_4]\text{PF}_6$ for the same length of time yielded primarily starting material and smaller amounts of mer- $[\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_3]\text{PF}_6$ and cis- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$. Longer irradiation time appears to produce decomposition and smaller yields of more highly substituted species.

In a reaction of peripheral interest, the isomer cis- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$ was unexpectedly obtained in a reaction of $\text{Mn}(\text{CO})_5\text{Cl}$ with an excess of CH_3NC . The reaction was run in CHCl_3 instead of THF, initiated by the contamination of a freshly prepared quantity of CH_3NC with CHCl_3 . The formation of the cis- L_4 isomer as the only product in quantitative yield differs considerably from the reaction sequence reported¹ when $\text{Mn}(\text{CO})_5\text{Br}$ is reacted with CH_3NC in THF where formation of $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2\text{Br}$ is followed by formation of $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$ and $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})]\text{Br}$. In CHCl_3 , the formation of $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2\text{Cl}$ is apparently followed by ligand displacement of the halide to give cis- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{Cl}$. This is even more surprising in light of the fact that several researchers^{10,11} have previously determined relative rates of substitutions for the species $\text{Mn}(\text{CO})_5\text{X}$ and found the order to be $\text{H} > \text{Cl} > \text{Br} > \text{I}$, thus $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2\text{Cl}$ should exchange a carbonyl faster than $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2\text{Br}$. It appears, therefore, that the formation of cis- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{Cl}$ in CHCl_3 is a function of the lower basicity of the

CHCl_3 . The more basic THF facilitates substitution of the fourth carbonyl to form $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Cl}$.

Finally, in view of the work in this chapter, it appears that the Pickett and Pletcher⁶ equation

$$E^\circ = A + x(dE^\circ/dx)_L + 1.48y$$

discussed in detail in Chapter I needs to be even further modified to include another parameter, although of lesser importance, defining complex geometry.

C. EXPERIMENTAL

All reactions were run under a nitrogen atmosphere. Infrared spectra, melting points, electrochemical data and elemental analyses were obtained as described in previous chapters.

Manganese tris(methyl isocyanide) dicarbonyl bromide, $\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_3\text{Br}$, manganese bis(methyl isocyanide) tricarbonyl bromide, $\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_2\text{Br}$, and the mer- and trans-isomers of manganese tris(methyl isocyanide) tricarbonyl hexafluorophosphate and manganese tetrakis(methyl isocyanide) dicarbonyl hexafluorophosphate, mer- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_3]\text{PF}_6$, and trans- $[\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})_2]\text{PF}_6$, were prepared as previously reported.¹

The approximate, nonparameterized molecular method has been described previously.⁷ All calculations were carried out using the MEDIEVAL series of programs written in these laboratories for the Univac 1110 computer at the Academic Computing Center, Madison, Wis.⁸

Preparation of cis- $[\text{Mn}(\text{CO})_2(\text{CNCH}_3)_4]\text{PF}_6$.

To a solution of $\text{Mn}(\text{CO})_2(\text{CNCH}_3)_3\text{Br}$ (0.31 g, 1.0 mmol) in ~50 ml THF was added AgPF_6 (0.40 g, 1.5 mmol). The solution was stirred at rt for 2h. The THF was then removed and the residue washed with dichloromethane. The solvent was again removed and 0.30 g of product crystal-

lized from acetone/ether as white cubes in 96% yield. The compound melts at 220-221 °C.

Anal. Calcd. for $C_{10}H_{12}N_4O_2F_6PMn$: C, 28.58; H, 2.88; N, 13.34.

Found: C, 29.03; H, 2.85; N, 13.72.

Preparation of fac-[Mn(CO)₃(CNCH₃)₃]PF₆.

To a solution of $Mn(CO)_3(CNCH_3)_2Br$ (1.4 g, 4.6 mmol) in ~50 ml THF was added a solution of $AgPF_6$ (1.5 g, 6.0 mmol) and CH_3NC (0.25 ml, 4.6 mmol) in ~25 ml THF. The reaction was stirred at rt for 1 h. The THF was removed and the residue washed with dichloromethane. The solution was evaporated again and 1.7 g of product crystallized from acetone/ether as white cubes in 88% yield. The compound melts at 167-168 °C.

Anal. Calcd. for $C_9H_9N_3O_3F_6PMn$: C, 26.55; H, 2.23; N, 10.32.

Found: C, 27.35; H, 2.33; N, 10.68.

Alternative Preparation of cis-[Mn(CH₃NC)₄(CO)₂]PF₆.

To a solution of $Mn(CO)_5Cl$ (10 g, 43 mmol) in 250 ml $CHCl_3$ was added an excess of CH_3NC (14 g, 340 mmol). The solution was refluxed for 22 h. The solvent was removed and 13 g of white product recrystallized from acetone-ether in near quantitative yield. The isolated complex has the same infrared spectrum as the aforementioned cis-[Mn(CH₃NC)₄(CO)₂]Cl.

Isomerization of cis-[Mn(CH₃NC)₄(CO)₂]PF₆.

A solution containing cis-[Mn(CH₃NC)₄(CO)₂]PF₆ (1.0 g, 2.4 mmol) in 100 ml CH₂Cl₂ was irradiated with a 100-watt General Electric Mercury Lamp for 2 h. The solvent was reduced and 0.25 g of a white precipitate filtered out. An infrared spectrum of the precipitate revealed a pattern identical to the known trans-[Mn(CH₃NC)₄(CO)₂]PF₆. Fractional crystallization of the filtrate yielded an additional 0.10 g of the trans isomer and 0.35 g of [Mn(CH₃NC)₅(CO)]PF₆.

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CHARACTERIZATION AND REACTIVITY OF ISOCYANIDE COMPLEXES OF MANG--ETC(U)
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TABLE 1. INFRARED DATA

Compound	$\nu(\text{CN})$	$\nu(\text{CO})$
<u>cis</u> -[Mn(CO) ₂ (CNMe) ₄]PF ₆ ^a	2230m, 2190s, 2170vs, 2150s	2000vs, 1975vs
<u>trans</u> -[Mn(CO) ₂ (CNMe) ₄]PF ₆ ^b	2177vs	1985vs
<u>fac</u> -[Mn(CO) ₃ (CNMe) ₃]PF ₆ ^a	2240m, 2210s, 2170w	2060vs, 2000vs, 1980m(sh)
<u>mer</u> -[Mn(CO) ₃ (CNMe) ₃]PF ₆ ^b	2245m, 2220sh, 2202s	2090m, 2020vs

(a) This work; CH₂Cl₂ solution, Beckman IR-10.

(b) Ref. 1; CH₂Cl₂ solution, Perkin Elmer 421.

TABLE 2. VOLTAMMETRIC DATA AND CALCULATED HOMO ENERGY VALUES

Compound	$1/2[E_{p,c} + E_{p,a}]^a$	$ E_{p,c} - E_{p,a} $	HOMO ENERGY ^b
<u>cis</u> -[Mn(CO) ₂ (CNMe) ₄]PF ₆	1.44v	200mv	-10.62 ev
<u>trans</u> -[Mn(CO) ₂ (CNMe) ₄]PF ₆	1.28v	270mv	-10.19 ev
<u>fac</u> -[Mn(CO) ₃ (CNMe) ₃]PF ₆	1.90v	200mv	-11.86 ev
<u>mer</u> -[Mn(CO) ₃ (CNMe) ₃]PF ₆	1.73v	270mv	-11.45 ev

(a) Cathodic and anodic peak potentials in volts vs SCE (aq KCl).
 Solutions in CH₂Cl₂ (5x10⁻³M) with Bu₄NClO₄ (0.1M) as supporting electrolyte. All processes are 1e oxidations (1); none meet the defined criterion for electrochemical reversibility, i.e.,
 $|E_{p,c} - E_{p,a}| < 0.059v$.

(b) Calculated by the method given in ref. 4.

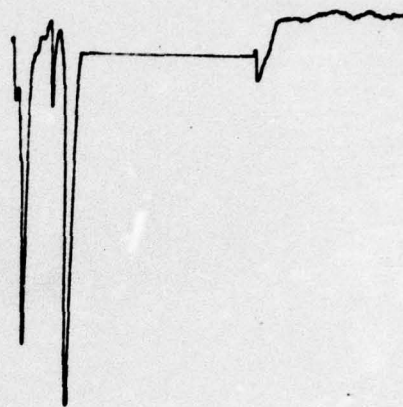
Figure 1

Infrared Spectra of Isomeric

 $\text{Mn(CO)}_{6-x}(\text{CH}_3\text{NC})_x^+$ ($x = 3, 4$) Complexes

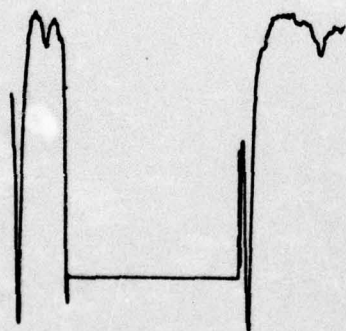


fac-[Mn(CH₃NC)₃(CO)₃]PF₆

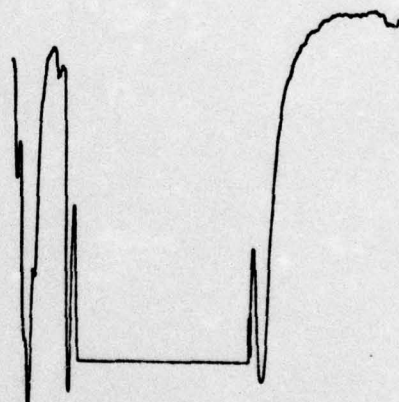


mer-[Mn(CH₃NC)₃(CO)₃]PF₆

trans-[Mn(CH₃NC)₄(CO)₂]PF₆



cis-[Mn(CH₃NC)₄(CO)₂]PF₆



2300 2000 1600
(CM⁻¹)

2300 2000 1600
(CM⁻¹)

Figure 2

Cyclic Voltammetry Curves for
 $\text{Mn}(\text{CO})_{6-x}(\text{CH}_3\text{NC})_x^+ (x = 3, 4)$ Isomers

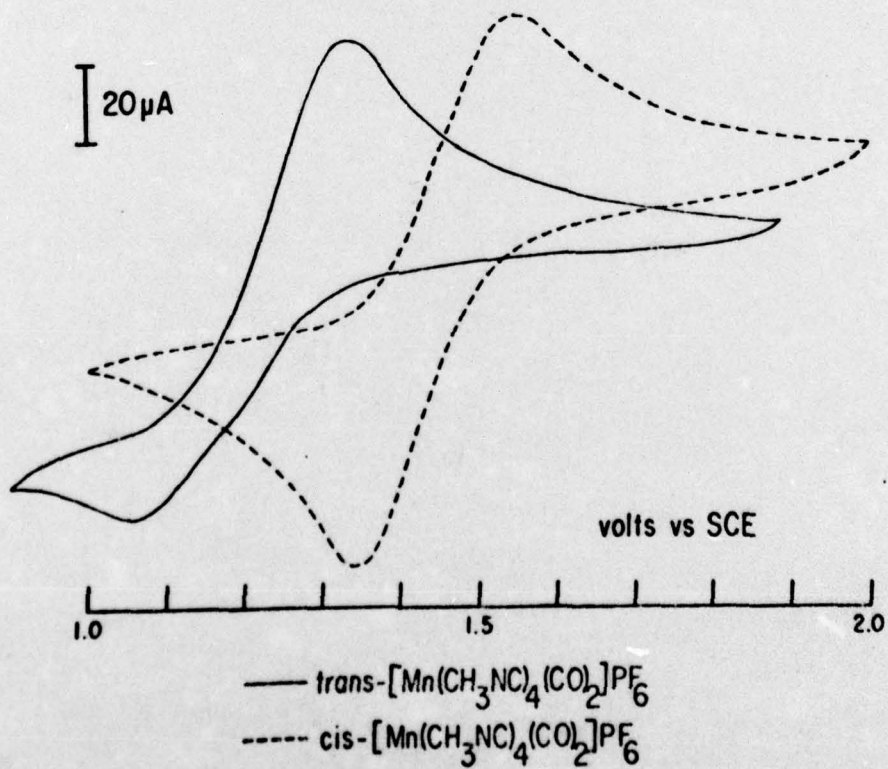
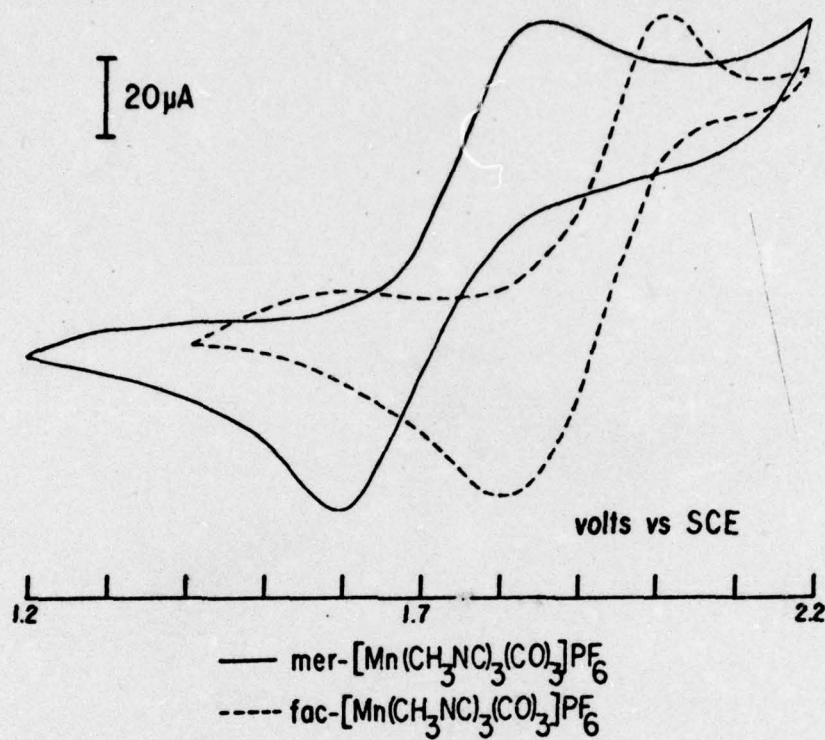
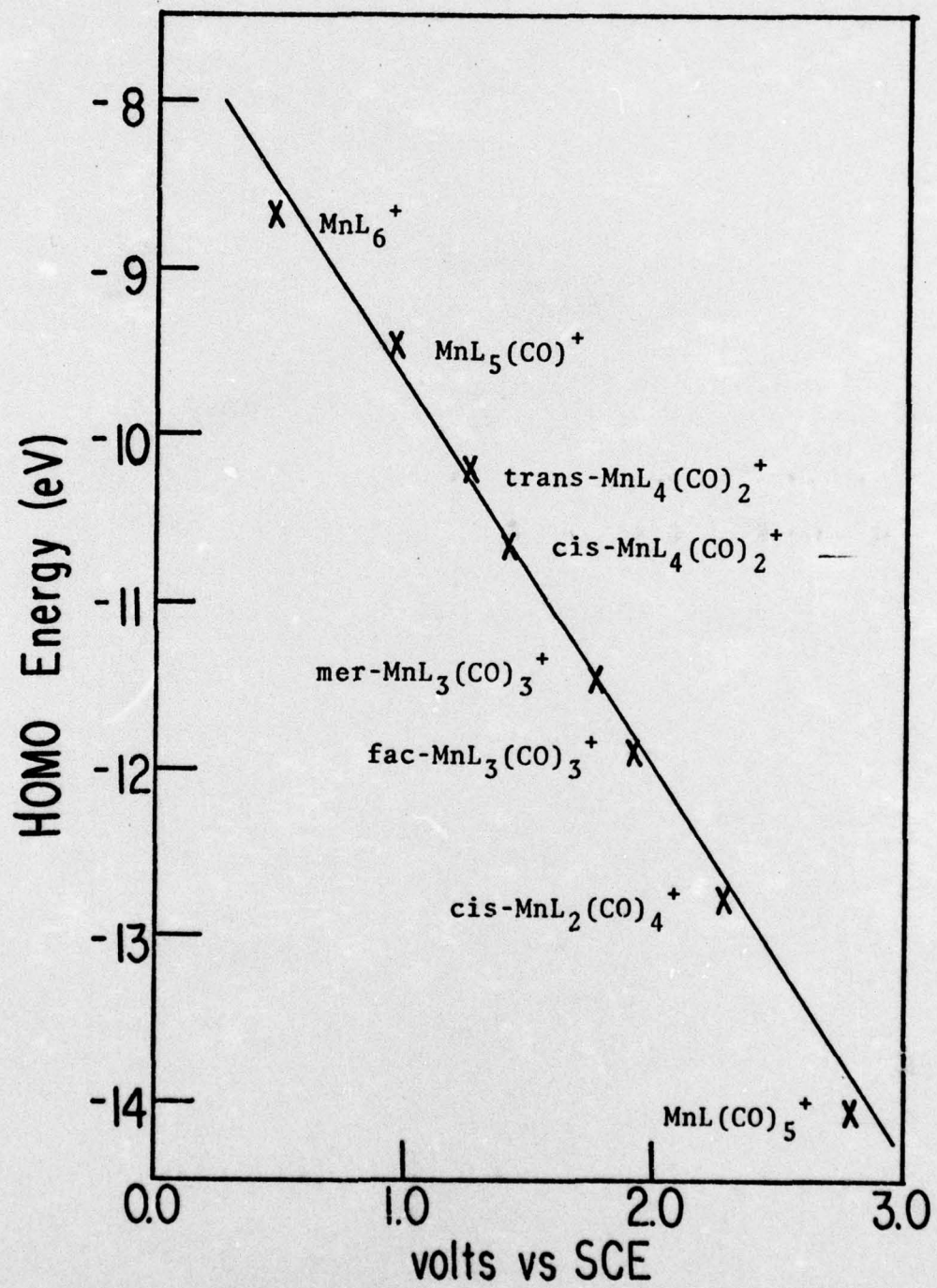


Figure 3

Correlation of $E_{1/2}$ Values with HOMO Energies for
the Series of Complexes $\text{Mn}(\text{CO})_{6-x}(\text{CH}_3\text{NC})_x^+$ ($x = 1-6$)



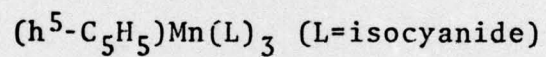
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13. I am indebted to Bruce Bursten of the research group of Dr. Richard F. Fenske not only for the molecular orbital calculations but also for many helpful discussions about the qualitative approach to this problem.

CHAPTER IV

SYNTHESIS, CHARACTERIZATION, AND ELECTROCHEMICAL

STUDIES OF MANGANESE(I) COMPLEXES OF THE FORM



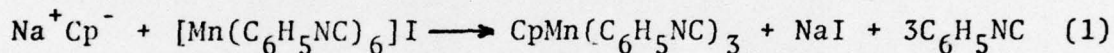
A. INTRODUCTION

Many researchers are continuing to devote extensive efforts toward the synthesis, characterization and study of reactivity of isocyanide complexes of metals, particularly with respect to determining ligand effects on the properties of the complex. Much of the effort is being directed toward the synthesis of isocyanide complexes which are analogous to previously known carbonyl complexes. Reactivity, electrochemical potential, and other comparisons between species such as $M(CO)_6$ and $M(CNR)_6$ ($M = Cr, Mo, W$), $Mn(CO)_6^+$ and $M(CNR)_6^+$, and complexes of the type $M(CO)_{6-x}(CNR)_x$ can be found in the literature.

Notably deficient, however, are literature references to the synthesis and characterization of isocyanide analogs of the cyclopentadienyl ($\eta^5-C_5H_5 = Cp$) or methylcyclopentadienyl ($\eta^5-CH_3C_5H_4 = MeCp$) metal complexes. Only a few Cp-metal carbonyl derivatives in which all of the carbonyls have been replaced by isocyanides have been reported. Included among these are $CpFe(CNR)_3^+$ ($R =$ phenyl or methyl),^{5,6} $[CpNi(C_6H_5NC)]_2$,⁷ $CpFe(CNC_6H_4OCH_3)_3^+$,⁸ $CpMn(C_6H_5NC)_3$,⁷ $CpFe(C_6H_5NC)_2X$ ($X = I, Br$),⁵ and $CpMo-(C_6H_5NC)_3Cl$.⁵ Adams and Cotton¹⁷ reported a structural

study on $(\text{CpNi}(\text{CH}_3\text{NC}))_2$ and high resolution infrared data on other complexes of the type $(\text{CpNi}(\text{RNC}))_2$ ($\text{R} = \text{C}_6\text{H}_5$, C_6H_{11} , CH_3 , CD_3 and $\text{CH}(\text{CH}_3)_2$) to show that all of the dimers are in the bridging configuration. In addition, a large number of partially substituted Cp-metal carbonyl complexes have been prepared.⁹ Among these, the anionic complex $\text{CpMo}(\text{CO})_2(\text{CNCH}_3)^-$ has been prepared by Adams¹⁸ by reduction of $\text{CpMo}(\text{CO})_2(\text{CH}_3\text{NC})\text{Cl}$ with Na/Hg amalgam in THF. Joshi, Pauson and Stubbs had previously reported the synthesis of the mixed species $\text{CpMo}(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})\text{I}$ and $\text{CpFe}(\text{CO})(\text{C}_6\text{H}_5\text{NC})\text{I}$. Fischer and Schneider¹⁰ reported the formation of $\text{CpMn}(\text{CO})_2(\text{CNH})$ on protonation of $\text{CpMn}(\text{CO})_2\text{CN}^-$. Mono-substituted derivatives of $[\text{CpMn}(\text{NO})(\text{CO})_2]^{+11}$ and disubstituted derivatives of $[\text{MeCpMn}(\text{NO})(\text{CO})_2]^{+12}$ were prepared by direct reaction with the isocyanide. Similar complexes of manganese with other hydrocarbon groups have also been reported. Walker and Mawby¹³ have reported reactions of π -arene- $\text{Mn}(\text{CO})_2\text{CN}$ (arene = mesitylene, C_6H_6) with HBF_4 to yield π -arene- $\text{Mn}(\text{CO})_2\text{CNBF}_3$ and with $[(\text{C}_2\text{H}_5)_3\text{C}]\text{BF}_4$ and $[(\text{C}_6\text{H}_5)_3\text{C}]\text{BF}_4$, to give $[\pi\text{-arene-Mn}(\text{CO})_2\text{CNR}]^+$ ($\text{R} = \text{C}_2\text{H}_5$, $-\text{C}(\text{C}_6\text{H}_5)_3$). Further, Smith¹⁴ has reported reactions of $[\text{C}_6\text{H}_6\text{Mn}(\text{CO})_3]\text{PF}_6$ with methyl isocyanide to give the mono and disubstituted species $[\text{C}_6\text{H}_6\text{Mn}(\text{CO})_{3-x}(\text{CH}_3\text{NC})_x]\text{PF}_6$ ($x=1,2$).

We decided to investigate the reactions of CpMn(CO)_3 with isocyanides in an attempt to synthesize complexes of the formula CpMn(RNC)_3 (R = alkyl or aryl isocyanide). In a review, Treichel⁹ had included the $\text{CpMn(CH}_3\text{NC)}_3$ complex among those unprepared complexes presenting a synthetic challenge and having a reasonable chance to exist. One such compound was known prior to this work. Pauson and Stubbs⁷ had previously reported the successful preparation of the complex $\text{CpMn(C}_6\text{H}_5\text{NC)}_3$.



We initially elected to pursue the same course, hoping to synthesize $\text{CpMn(CH}_3\text{NC)}_3$ by the reaction of Na^+Cp^- with $[\text{Mn(CH}_3\text{NC)}_6]\text{I}$. Unfortunately, we were totally unsuccessful in even duplicating the work of Pauson and Stubbs and became somewhat skeptical about this work, which had appeared only as an initial communication; no other reports of successful preparations of CpMn(L)_3 (L = isocyanide) complexes have appeared nor has a full paper on this work appeared.

A report by Müller and Herberhold,¹⁵ which included an examination of the mass spectra of a number of $\text{CpMn(CO)}_2\text{L}$ complexes, stated that substituted derivatives of CpMn(CO)_3 could only be prepared by photolysis since CpMn(CO)_3 is resistant to substitution at temperatures over

200 °C. Only a few photolysis experiments have been successful in displacing all three carbonyls. The first occurred when CpMn(CO)_3 was irradiated in benzene to form CpMnC_6H_6 . More recently, a paper by Dineen and Pauson⁶ reported some interesting results from the photolysis of MeCpMn(CO)_3 with cyanide. Among the reaction products listed are crude $\text{K}_3[\text{MeCpMn(CN)}_3]$, which was alkylated to $\text{K}_2[\text{MeCpMn(CNC}_2\text{H}_5)(\text{CN})_2]$ and $\text{K}[\text{MeCpMn(CNC}_2\text{H}_5)_2(\text{CN})]$; also $\text{K}[\text{MeCpMn(CO)}_2(\text{CN})]$ which was protonated and alkylated to $\text{MeCpMn(CO)}_2(\text{CNH})$ and $\text{MeCpMn(CO)}_2(\text{CNC}_2\text{H}_5)$. Also, Butler and Fenster³¹ reported an interesting stepwise preparation of CpMn(CS)_3 by photolytic substitution of C_8H_{14} for CO followed by reaction with CS_2 .

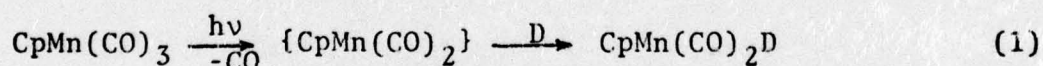
In view of the fact that photolysis has now become an established method of synthesis for complexes of the type $\text{CpMn(CO)}_{3-x}(\text{L})_x$, we decided to attempt to prepare at least the $\text{CpMn(aryl isocyanide)}_3$ complexes by photolysis of CpMn(CO)_3 in THF in the presence of excess ligand.

By this route, we have successfully prepared a series of CpMn(CNR)_3 complexes where $\text{R} = \text{C}_6\text{H}_5$, CH_3 , $p\text{-ClC}_6\text{H}_4$, and Cl_5C_6 . The synthesis, spectral properties, electrochemical behavior, and reactivity were examined and the obvious comparison with CpMn(CO)_3 made. Further, we reexamined

the nucleophilic attack on isocyanide complexes of manganese (I) with Cp^- by changing reactants and conditions and in at least one case were successful in preparing a complex of the type $\text{CpMn(CO)}_{3-x}\text{L}_x$.

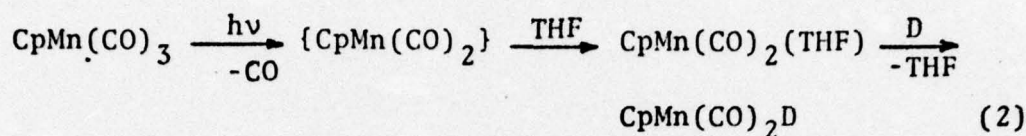
B. RESULTS AND DISCUSSION

The ultraviolet irradiations of CpMn(CO)_3 were all run in THF with a small excess of ligand, monitoring the reaction by periodic infrared spectra until no further change in the $\nu(\text{CN})$ or $\nu(\text{CO})$ region (2200cm^{-1} - 1800cm^{-1}) was observed. A standard General Electric Mercury Lamp was used as the ultraviolet source and the irradiation was done in Pyrex glassware. Shortly after a typical reaction was started (2 to 3 minutes), it was noted that the solution changed from yellow to bright red and then back to yellow. Strohmeier¹⁹, who has been the acknowledged pioneer in the area of ligand displacement reactions by ultraviolet radiation, has noted a similar phenomenon in his irradiations of CpMn(CO)_3 . During his studies, he formulated the following reaction scheme



where D represents an electron-donating ligand and $\{\text{CpMn(CO)}_2\}$ represents the non-isolable acceptor intermediate having an empty orbital. He has further determined that the stability of the Mn-D bond in the complex $\text{CpMn(CO)}_2\text{D}$ should therefore be a function of the donor strength of the ligand D. By observing reactions of various $\text{CpMn(CO)}_2\text{D}$ complexes with strong acceptors such as I_2 , BF_3 , and $\text{B(CH}_3)_3$,

relative donor strengths of D were determined. When D is tetrahydrofuran, the Mn-D bond strength is weak and the complex $\text{CpMn(CO)}_2(\text{THF})$ can not be isolated, whereas a variety of monosubstituted amine complexes have been isolated as air-stable red crystals. The red solution we noted after a few minutes of radiation time can therefore be explained as the initial formation of the complex $\text{CpMn(CO)}_2(\text{THF})$ and the change back to yellow as the substitution of isocyanide for THF. To further examine this phenomenon, we irradiated a solution of CpMn(CO)_3 in THF in the absence of ligand. The solution remained red during the entire radiation period, decayed slowly to the original pale yellow solution and exhibited slight decomposition after the irradiation was stopped. Another CpMn(CO)_3 solution was irradiated for about 30 minutes in the absence of ligand. Addition of the isocyanide resulted in the immediate disappearance of the red color and appearance of a yellow solution. The appearance of the red solution even while irradiating in the presence of isocyanide is probably a function of the higher concentration of THF compared to the relatively small amount of isocyanide. The following reaction sequence can be used to describe the irradiation of CpMn(CO)_3 in THF in the presence of a stronger donor ligand than THF.



After the rapid formation of the monosubstituted isocyanide complex, removal of the remaining carbonyls requires between 24 and 96 hours of irradiation time.

The isocyanide ligands we chose for this project encompassed a wide range of π -acceptor strengths according to the sequence $\text{C}_6\text{Cl}_5\text{NC} > p\text{-ClC}_6\text{H}_4\text{NC} > \text{C}_6\text{H}_5\text{NC} > \text{CH}_3\text{NC}$. Interestingly, we also irradiated a THF solution of CpMn(CO)_3 in the presence of $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC}$ for ~48 hours but were unable to isolate any product. In an attempt to explain this phenomenon in light of the good yields achieved with the other isocyanides, we note some recent research by Ramakrishnan and Boyer.^{20,21} These researchers have examined the ultraviolet irradiations of various aryl isocyanides in solution and noted that they isomerize to the cyanide ($\text{RNC} \xrightarrow{h\nu} \text{RCN}$), and further that the tendency to isomerize is greatly enhanced by the presence of a strong electron donor group (such as the $\text{CH}_3\text{O-}$ group) in the para position. Also, although all aryl isocyanides were found to isomerize to a certain extent, this extent increased in protic solvents such as CH_3OH and was considerably slowed in aprotic solvents such as THF.

Special comment should be made about the reactions of CpMn(CO)_3 with CH_3NC . Our initial reaction was attempted using a CpMn(CO)_3 to CH_3NC stoichiometric ratio of $\sim 1:2$. The complex isolated on evaporation of solvent showed a single strong, broad carbonyl absorption, $\nu(\text{CO})$, at 1870 cm^{-1} and isocyanide absorptions, $\nu(\text{CN})$, at 2120 and 2070 cm^{-1} . We noted, however, that even in the solid state the complex displayed a rapid decomposition rate as evidenced by the gradual darkening of the complex and the constant evolution of free methyl isocyanide. After several unsuccessful attempts to obtain a pure product, the solid residue was sublimed and a yellow air-stable complex collected on the probe. Surprisingly, an infrared spectrum revealed a completely different pattern, one which showed two intense carbonyl absorptions, $\nu(\text{CO}) = 1950, 1890\text{ cm}^{-1}$, and one equally intense isocyanide absorption, $\nu(\text{CN}) = 2150\text{ cm}^{-1}$, (Table 1). This pattern is nearly identical to the spectra of the complexes $\text{CpMn(CO)}_2(\text{CNC}_6\text{H}_{11})^{16}$ and $\text{CH}_3\text{Cp-Mn(CO)}_2(\text{CH}_3\text{NC})^{16}$ (Table 1). It is apparent therefore that some type of solid state rearrangement occurs in which decomposition of the disubstituted complex supplies a carbonyl ligand to substitute for an isocyanide in another disubstituted molecule to form the stable monosubstituted species.

When the irradiation was run with sufficient ligand to displace all three carbonyls, the crude product was initially isolated in reasonable yield (46%). It soon became apparent that even trace amounts of air caused the complex to rapidly decompose. Reasonably pure product was obtained by precipitation from THF with heptane if the solvents were thoroughly deaerated and all work-up and recovery was carried out in an oxygen free environment, e.g., nitrogen dry box and Schlenk apparatus. The instability of the complex to oxidation was not unexpected, particularly in light of the fact that both Cp^- and CH_3NC are poor π -acceptors. The metal, therefore, is expected to be very electron rich and susceptible to air oxidation. Quantitative support for this was obtained electrochemically and will be presented later in this discussion.

The infrared spectra of the $\text{CpMn}(\text{RNC})_3$ complexes turned out to be unusual and deserve an attempted explanation. The spectra of $\text{CpMn}(\text{RNC})_3$ aryl isocyanide complexes all exhibited a sharp single A_1 mode absorption at $\sim 2070 \text{ cm}^{-1}$ and a broad, ill-defined E mode absorption below 2000 cm^{-1} (Table 1). The same phenomenon arose whether in CH_2Cl_2 solution or nujol mull. Even when the products were repeatedly recrystallized and found to be pure by elemental analyses and sharp melting points, the absorp-

tion below 2000 cm^{-1} remained broad, extending across 200 cm^{-1} at half peak height when the peak had an intensity of 8 on a maximum scale of 10. Recent observations by other researchers may have shed some light on this phenomenon. An early reference by Cotton and Zingales²² attempted to rationalize the existence of more than the one expected infrared peak and the broadness of the absorptions in a series of $\text{Cr}(\text{RNC})_6$ complexes on the basis of significant asymmetric bending of each RNC group. More recently, Treichel and Essenmacher²³ have shown that these same $\text{Cr}(\text{RNC})_6$ complexes exhibit a single sharpened absorption, $\nu(\text{CN})$, at higher energy when oxidized to the 17 e^- $[\text{Cr}(\text{RNC})_6]\text{PF}_6$ species. In an attempt to explain this phenomenon and relate it to the broadening exhibited by our $\text{CpMn}(\text{aryl isocyanide})_3$ complexes, we offer the following qualitative rationalization.²⁴ The aromatic ring on the aryl isocyanides exhibits C-C multiple bond stretching absorption²⁵ between 1450 and 1600 cm^{-1} and the energy of these absorptions is unaffected by changes in $\nu(\text{CN})$. When the aryl isocyanides are forced to accept a greater share of the electrons donated by the metal, as is the case in the $\text{CpMn}(\text{RNC})_3$ complexes, the $\nu(\text{CN})$ are lowered in energy (Table 1). This in turn brings these absorptions close enough to the C-C multiple bond stretches to create

mixing of the vibrational modes and subsequent broadening of the bands or creation of new bands. This could account for the sharpening and simplification of the $\nu(\text{CN})$ absorption pattern in going from $\text{Cr}(\text{RNC})_6$ to $\text{Cr}(\text{RNC})_6^{+2}$ since the $\nu(\text{CN})$ band is progressively further removed from the ring stretching frequencies. Additional support for this theory is shown by the infrared spectrum of $\text{CpMn}(\text{CH}_3\text{NC})_3$ which does not exhibit the same broadened pattern shown by the aryl isocyanide complexes and would not be expected to do so in view of the absence of other high energy modes with which the $\nu(\text{CN})$'s could mix. It should be noted, however, that the infrared spectrum of $\text{CpMn}(\text{CH}_3\text{NC})_3$ does not exhibit the recognizable sharp A_1 and broad E modes shown for a typical C_{3v} ML_3 fragment in solution.²⁶ The complex $\text{CpMn}(\text{CO})_3$ does exhibit split E mode absorption when the spectrum is taken in a KBr mull. The $\text{CpMn}(\text{CH}_3\text{NC})_3$ complex shows a sharp peak at 2100 cm^{-1} and two broader, more intense absorptions at 2030 and 1950 cm^{-1} , a pattern which might best be explained by assuming that the normally observed degeneracy of the E mode in solution spectra has been removed and the frequencies of the E mode absorptions further separated. In light of these infrared spectra complications, it should come as no surprise that identification of these products by infrared

alone turned out to be impossible. In fact, initial examination of the spectra led us to believe we had not succeeded in replacing all of the carbonyls. Fortunately, other analytical tools were available and proton magnetic resonance spectra were particularly enlightening in assigning the correct stoichiometry.

The complexes $\text{CpMn}(\text{RNC})_3$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-ClC}_6\text{H}_4$) and $\text{CpMn}(\text{CO})_2(\text{CH}_3\text{NC})$ were sufficiently soluble in CDCl_3 to run their nmr spectra in that solvent. In the case of the $\text{CpMn}(\text{CH}_3\text{NC})_3$ complex, limited solubility and instability in most common deuterated solvents led us to use CS_2 . Interestingly, the CS_2 solution turned deep red when the complex was added, but an infrared spectrum of the solution indicated that the $\nu(\text{CN})$ absorption pattern was identical to that shown by the complex in the pale yellow CH_2Cl_2 solution. The nmr spectra were simplified by the good separation of phenyl, methyl and cyclopentadienyl proton peaks which were singlets in most cases (Table 1). It was therefore easy to obtain accurate integrations which convinced us that we had in fact prepared the fully substituted species.

By far the most significant and interesting information about the new complexes came from the electrochemical studies. The complexes $\text{CpMn}(\text{RNC})_3$ ($\text{R} = \text{CH}_3$, C_6H_5 , $p\text{-ClC}_6\text{H}_4$)

all exhibited reasonably reversible $1e^-$ oxidations for the process $\text{CpMn(RNC)}_3 \xrightleftharpoons[\text{-e}^-]{\text{+e}^-} \text{CpMn(RNC)}_3^+$ (Table 2, Figures 1 and 2) based on the symmetry of the oxidation and reduction scans as opposed to the normally accepted reversibility criterion, i.e. $|E_{p,c} - E_{p,a}| < .059 \text{ v.}$ This reversibility argument was discussed in greater detail in Chapter I. These complexes also displayed second oxidation peaks for the process $\text{CpMn(RNC)}_3^+ \xrightarrow{-e^-} \text{CpMn(RNC)}_3^{+2}$ which were found to be totally irreversible as evidenced by the absence of the cathodic current indicating probable decomposition of the complex after the second oxidation, (Figure 1,2). The complex $\text{CpMn(CH}_3\text{NC)}_3$ shows the appearance of a reduction peak at ~ -0.8 volts (Figure 2) which is evident only if the solution is scanned past the second oxidation potential. It is therefore apparent that the second oxidation produces a totally different species which then also exhibits a different reduction potential. The $E_{1/2}$ values for the first oxidation of these trisubstituted complexes produced no surprises. The values were directly proportional to the ability of the ligand to accept electron density from the metal and furthermore helped to explain the relative stabilities of the complexes to air oxidation. The aryl isocyanide complexes appear to be stable indefinitely in the solid state although the complexes CpMn(RNC)_3

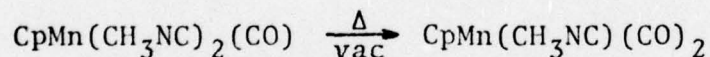
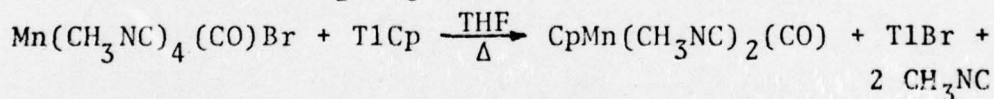
(R = C₆H₅ and p-ClC₆H₄) decompose rapidly in solution if the solvents are not deaerated. The CpMn(C₆Cl₅NC)₃ complex appears to be both air and solution stable and the air-sensitivity of the CpMn(CH₃NC)₃ complex has been previously mentioned. These stabilities can be easily explained by the range of oxidation potentials reported. We have previously shown⁴ that successive exchange of CH₃NC for CO in the series of complexes Mn(CO)_{6-x}(CH₃NC)_x⁺ resulted in the stepwise reduction of the E_{1/2} values by ~0.5 volts. The complexes CpMn(CO)_{3-x}(CH₃NC)_x show a similar but slightly larger stepwise change in oxidation potentials as x increases (Table 2). The E_{1/2} for the complex CpMn(CO)₃ was found to be 1.41 volts vs SCE in CH₂Cl₂ while the E_{1/2} for CpMn(CH₃NC)₃ was found to be -0.30 volts. The E_{1/2} for the monosubstituted complex CpMn(CH₃NC)(CO)₂ was found to be 0.74 volts. It is apparent therefore that the change in oxidation potential is not nearly as linear as in the case of the octahedral Mn(CO)_{6-x}(CH₃NC)_x⁺ complexes. This is not surprising in view of the fact that only three carbonyl ligands and likewise three isocyanide ligands are accepting the major portion of the electron donation from the metal. It is also apparent, based on the low energy ν(CN) absorptions, that the methyl isocya-

nides are receiving a greater share of the electron density in the $\text{CpMn}(\text{CH}_3\text{NC})_3$ complex than in the octahedral complexes. Therefore, stepwise substitution of CH_3NC for CO is shown to have a progressively smaller effect on the $E_{1/2}$ value, evidenced by the non-linearity of the potential vs the number of carbonyls in progressing from $\text{CpMn}(\text{CO})_3$ to $\text{CpMn}(\text{CH}_3\text{NC})_3$.

The complex $\text{CpMn}(\text{C}_6\text{Cl}_5\text{NC})_3$ showed only one oxidation peak when scanned through the range $-2.0 \rightarrow +2.0$ volts. A single oxidation at $E_{1/2} = 0.65$ v. vs SCE. This is not surprising in view of the relatively high electron withdrawing power of the C_6Cl_5 group.

Finally, as a result of our successes through the use of ultraviolet radiation, we were able to isolate the compound $\text{CpMn}(\text{C}_6\text{H}_5\text{NC})_3$ which Pauson and Stubbs⁷ had reportedly prepared many years earlier. They had unfortunately reported only the color and melting point of the complex, but the similarities of these data with the melting point and color of our trisubstituted complex led us to believe that they had in fact succeeded in reacting $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6^+$ with Cp^- to produce the complex. With this in mind, we were still determined to prepare the $\text{CpMn}(\text{RNC})_3$ complexes by the same method. However, we have found in our research that the MnL_6^+ complexes are remarkably

stable and reactively inert, and in all of our reactions of Mn(RNC)_6^+ with Na^+Cp^- , we successfully recovered the MnL_6^+ starting material. At the same time, we had found that complexes of the type $\text{Mn(CO)}_{5-x}(\text{RNC})_x\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) were susceptible to nucleophilic attack by a variety of anions (CN^- , Mn(CO)_5^- , see Chapters 2, 3, 5, 6). We also sought more convenient ways of using the Cp^- anion which is highly reactive when prepared by Na reduction. We found that several researchers²⁷ had been using the compound Tl^+Cp^- , a stable solid which can be easily handled. We therefore reacted $\text{Mn(CO)(CH}_3\text{NC)}_4\text{Br}$ with Tl^+Cp^- in refluxing THF. Sublimation of the residue after solvent removal resulted in the isolation of a yellow complex having the same infrared and nmr spectra as the previously mentioned $\text{CpMn(CO)}_2(\text{CH}_3\text{NC})$.



Apparently, the same type of solid state rearrangement as that previously mentioned in the reaction of CpMn(CO)_3 with a deficiency of CH_3NC takes place here.

We have shown, therefore, that formation of CpMn(RNC)_3 complexes can be prepared by nucleophilic attack on $\text{Mn(CO)}_{5-x}(\text{RNC})_x\text{X}$ complexes with Cp^- . However, preparation

of these complexes by ultraviolet radiation of CpMn(CO)_3 in the presence of ligand was found to be by far the easiest and most efficient synthetic approach.

C. EXPERIMENTAL

All reactions were carried out under nitrogen. Melting points were determined using a Thomas-Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were taken on a Beckman IR-10 spectrometer. Nuclear magnetic resonance spectra were taken on a Varian A-60 60 MHz or JEOL MH-100 100 MHz instrument using CS_2 or CDCl_3 as solvents and tetramethylsilane as an internal standard. Elemental analysis were performed by Galbraith laboratories, Inc., Knoxville, Tennessee. Infrared and proton magnetic resonance data are reported in Table 1. Electrochemical data was obtained as reported in previous chapters.

Cyclopentadienylmanganese tricarbonyl was prepared by the method of Cordes and Neubauer.²⁸ Phenyl isocyanide, p-chlorophenyl isocyanide, and pentachlorophenyl isocyanide were all prepared by the method of Appel, Kleinstück and Ziehn.²⁹ Methyl isocyanide³⁰ was prepared by the method of Schuster, Scott, and Casanova. Bromocarbonyl tetrakis(methyl isocyanide) manganese(I), $\text{Mn}(\text{CO})(\text{CH}_3\text{NC})_4\text{Br}$, was prepared by the method of Treichel, Dirreen and Mueh⁴.

Preparation of $h^5-C_5H_5Mn(C_6H_5NC)_3$.

To a solution of $h^5-C_5H_5Mn(CO)_3$ (2.0 g, 10 mmol) in 100 ml THF in a 250-ml three-necked Pyrex flask fitted with condenser was added C_6H_5NC (4.5 g, 44 mmol). The solution was irradiated with a 100-watt General Electric Mercury Lamp for 48 h. The solvent was evaporated and the residue washed with several 100 ml portions of hexane. The hexane was removed and 3.0 g of orange cubes were crystallized from deaerated acetone-hexane in 70% yield. The compound decomposes in solution and melts at 100 °C.

Anal. Calcd. for $C_{26}H_{20}N_3Mn$: C, 72.72; H, 4.70; N, 9.79.

Found: C, 72.63; H, 4.66; N, 9.83

The following compounds were prepared by the same route.

$h^5-C_5H_5Mn(p-ClC_6H_4NC)_3$.

Obtained as bright yellow needles from acetone-ether in 75% yield after 96 h irradiation time, solvent evaporation, and sublimation at 50° to remove unreacted $p-Cl-C_6H_4NC$. The compound melts at 132 °C.

Anal. Calcd. for $C_{26}H_{17}N_3Cl_3Mn$: C, 58.62; H, 3.22; N, 7.89.

Found: C, 58.33; H, 3.09; N, 7.79.

$h^5-C_5H_5Mn(Cl_5C_6NC)_3$.

The solution was irradiated for 27 h, the THF solvent was removed and the residue washed with acetone leaving

red-orange crystals behind. The product was recrystallized as red cubes from toluene- CHCl_3 in 34% yield. It melts at 270 °C.

Anal. Calcd. for $\text{C}_{26}\text{H}_5\text{N}_3\text{Cl}_{15}\text{Mn}$: C, 33.00; H, 0.53; N, 4.44.

Found: C, 32.98; H, 0.41; N, 4.38.

$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CH}_3\text{NC})_3$.

Obtained as yellow air sensitive crystals from THF-heptane in 46% yield after 29 h irradiation time. The compound melts at 148-150 °C in a sealed capillary tube.

Anal. Calcd. for $\text{C}_{11}\text{H}_{14}\text{N}_3\text{Mn}$: C, 54.33, H, 5.80; N, 17.28

Found: C, 55.24; H, 5.32; N, 16.09.

Reaction of $\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ and CH_3NC .

To a solution of $\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3$ (4.0 g, 20 mmol) in 100 ml THF was added CH_3NC (1.8 g, 44 mmol). The solution was irradiated for 18 h and the solvent evaporated. The residue was found to be air-sensitive so all crystallization attempts were performed under N_2 in deaerated solvents. In spite of these precautions, periodic solution infrared spectra revealed changing patterns. The residue was finally sublimed to yield the only isolable product, 1.0 g $\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})$, identified by infrared and nmr spectra. The compound melts at 92 - 93 °C.

Attempted Preparation of $h^5-C_5H_5Mn(CH_3NC)_2(CO)$.

To a solution of $Mn(CO)(CH_3NC)_4Br$ (1.5 g, 4.6 mmol) in 100 ml THF was added $Tl(C_5H_5)$ (1.5 g, 5.6 mmol). The solution was refluxed for 12 h, the precipitate was removed by filtration and discarded, and the remaining red solution was evaporated to dryness. The residue was sublimed at $\sim 50^\circ$ for 12 h yielding 0.20 g of yellow crystals which had the same infrared and nmr spectra and melting point as the previously mentioned $h^5-C_5H_5Mn(CO)_2(CH_3NC)$.

TABLE 1. INFRARED AND PROTON MAGNETIC RESONANCE DATA

Compound	IR Spectral Data (cm ⁻¹) ^a		NMR ^d
	$\nu(\text{CN})$	$\nu(\text{CO})$	$\tau(\text{Intensity})$
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CH}_3\text{NC})_3$	1950m(br), 2030s 2100m		5.96s(5) 6.80s(9)
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{C}_6\text{H}_5\text{NC})_3$	2070m, 1955s(vbr)		3.00s(15) 5.50s(5)
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_3$	2070m, 1955s(br)		3.00m(12) 5.43s(5)
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{ClC}_5\text{C}_6\text{NC})_3$	2060m, 1915s(vbr)		
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CH}_3\text{NC})(\text{CO})_2$	2150m	1950s, 1890s	5.60s(5) 6.67s(3)
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_3^b$		2020s, 1934s 1912s	6.04s(5) ^b
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{CNH})^b$	2016s	1919s, 1859s	5.83s(5) ^b 5.18s(1)br
$\text{h}^5\text{-CH}_3\text{C}_5\text{H}_4\text{Mn}(\text{CO})(\text{CH}_3\text{NC})^c$	2180	1945, 1896	5.6s(4) 8.1s(3), 6.2s(3)
$\text{h}^5\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2(\text{CNC}_6\text{H}_{11})^c$	2120	1949, 1896	

TABLE 1. (Contd.)

- a) IR spectra in CH_2Cl_2 unless otherwise noted.
- b) Ref. 10; spectra as KBr pellets. NMR spectra in C_6D_6 .
- c) Ref. 16; spectra as Nujol mulls.
- d) Spectra in CDCl_3 unless otherwise noted.

TABLE 2. VOLTAMMETRIC DATA

Compound	$1/2[E_{p,c} + E_{p,a}]^a$	$ E_{p,c} - E_{p,a} $	Process
$h^5-C_5H_5Mn(C_6H_5NC)_3$	0.13 $1.12(E_{p,a})^b$	180mV	$+1 \longrightarrow +2$ $+2 \longrightarrow +3$
$h^5-C_5H_5Mn(p-ClC_6H_4NC)_3$	0.22 $1.05(E_{p,a})^b$	220mV	$+1 \longrightarrow +2$ $+2 \longrightarrow +3$
$h^5-C_5H_5Mn(Cl_5C_6NC)_3$	0.65	100mV	$+1 \longrightarrow +2$
$h^5-C_5H_5Mn(CH_3NC)_3$	-0.30 $0.72(E_{p,a})^b$ $1.80(E_{p,a})^b$	210mV	$+1 \longrightarrow +2$ $+2 \longrightarrow +3$ $+3 \longrightarrow +4$
$h^5-C_5H_5Mn(CO)_3$	1.41	300mV	$+1 \longrightarrow +2$
$h^5-C_5H_5Mn(CO)_2(CH_3NC)$	0.74	260mV	$+1 \longrightarrow +2$

a) Cathodic and anodic peak potentials in volts vs SCE (aq. KCl).

Solutions in CH_2Cl_2 (5×10^{-3} M) with Bu_4NClO_4 (0.1 M) as supporting electrolytes. All processes are le oxidations; none meet the defined criterion for electrochemical reversibility, i.e., $|E_{p,c} - E_{p,a}| > 0.059$ v, but all $+1 \longrightarrow +2$ processes are well-behaved, $|i_{p,a}| \approx |i_{p,c}|$, and peak separation can be decreased by slowing the scan rate.

b) Only the oxidation peak is well defined for these processes.

Figure 1

Cyclic Voltammetry of
 $\text{h}^5\text{-C}_5\text{H}_5\text{Mn(RNC)}_3$ (R = CH_3 , p- ClC_6H_4)

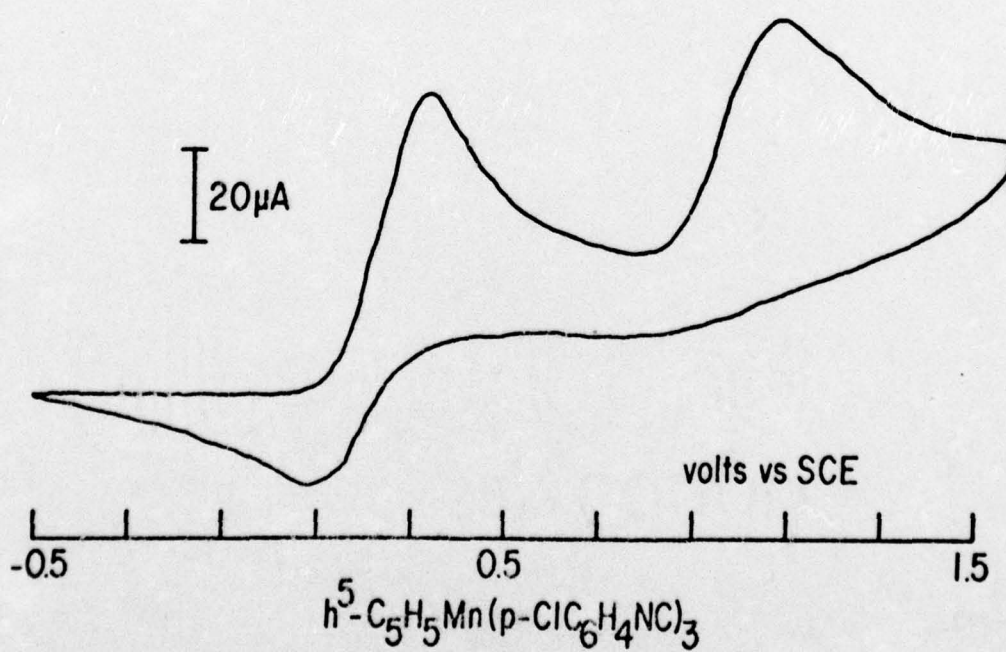
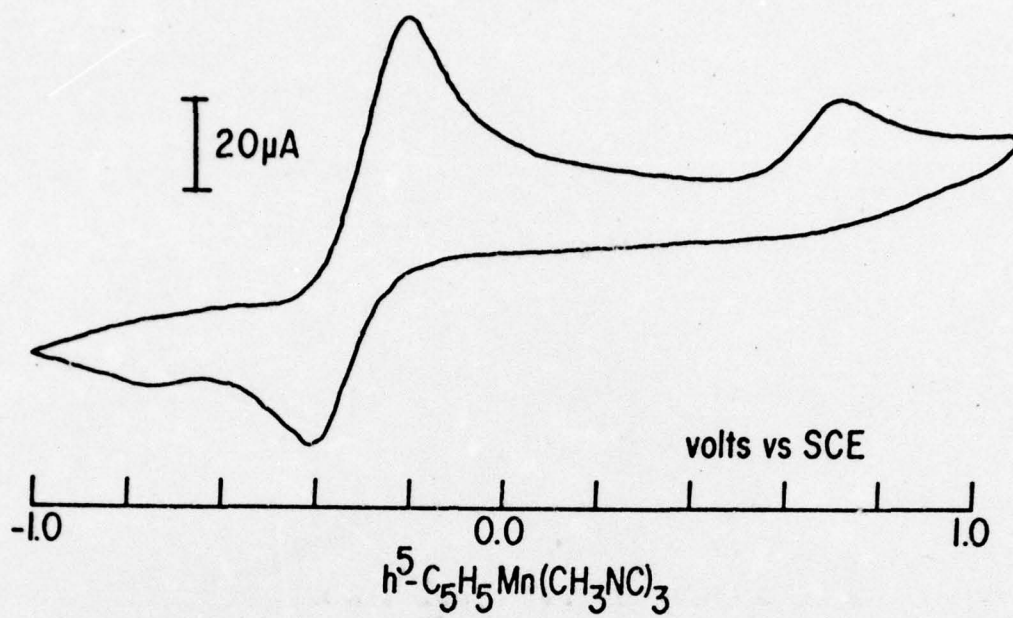
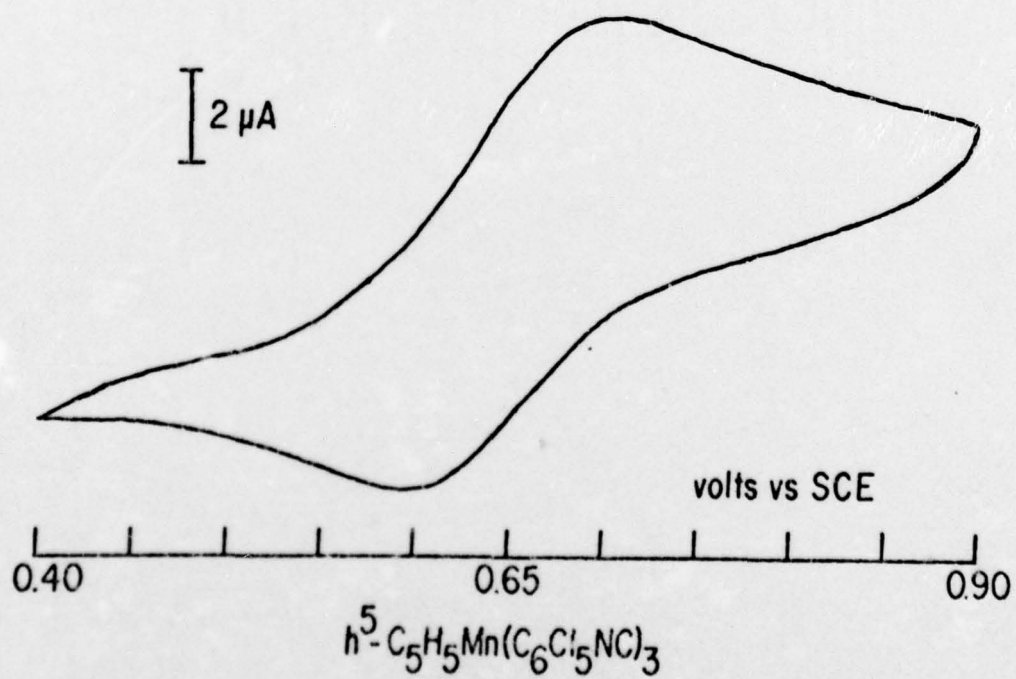
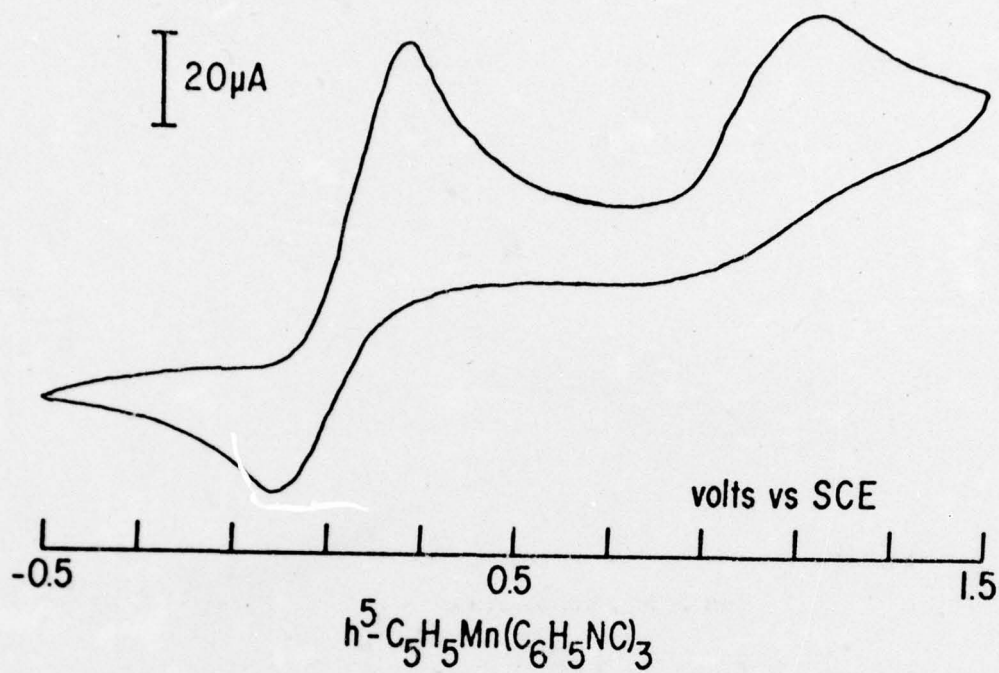


Figure 2

Cyclic Voltammetry of
 $\text{h}^5\text{-C}_5\text{H}_5\text{Mn(RNC)}_3$ (R = C_6H_5 , C_6Cl_5)



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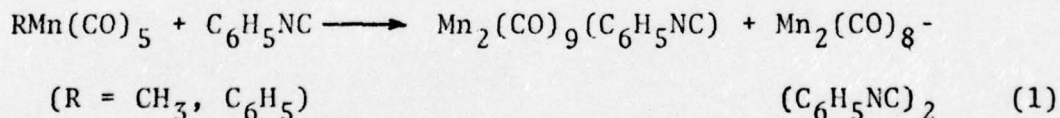
CHAPTER V

SYNTHESIS AND CHARACTERIZATION OF
ISOCYANIDE COMPLEXES OF MANGANESE (0)

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ISOCYANIDE COMPLEXES OF MANGANESE (0)

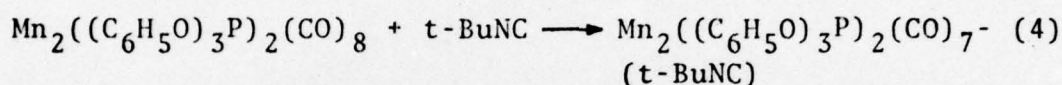
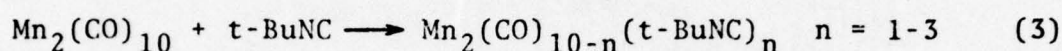
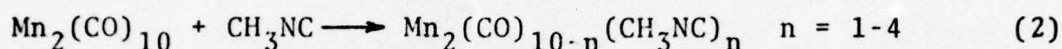
A. INTRODUCTION

A relatively small amount of effort has been directed toward the synthesis, characterization and reactivity of zero valent isocyanide complexes of manganese. Only a few researchers have shown interest in this area, and only a few compounds have been reported. An early reference by Joshi, Pauson and Stubbs (JPS)¹ presented the synthesis and characterization of the complexes $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$ and $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$. Interestingly, these complexes were recovered unexpectedly in low yields in the reaction of methyl- and phenyl-pentacarbonylmanganese with phenyl isocyanide.

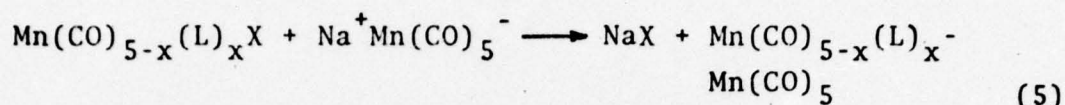


The authors had expected the formation of the acyl derivatives $\text{CH}_3\text{COMn}(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})$ and $\text{C}_6\text{H}_5\text{COMn}(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})$. More recently, Adams and Chodos² prepared the complex $\text{Mn}_2(\text{CO})_7(\text{CH}_3\text{NC})_3$ by irradiation of $\text{Mn}_2(\text{CO})_{10}$ in the presence of CH_3NC in order to study the variable temperature PMR behavior of this species. This complex had been prepared earlier by Treichel and Dirreen³ by refluxing $\text{Mn}_2(\text{CO})_{10}$ and CH_3NC

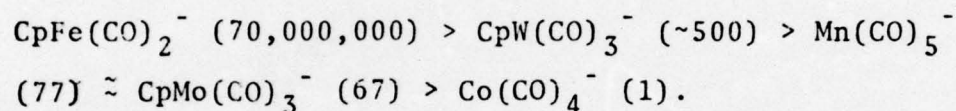
in THF. Even more recently, Grant, Newman and Manning⁴ reported the preparation of $\text{Mn}_2(\text{CO})_{10-n}(\text{RNC})_n$ ($\text{R} = \text{CH}_3$, $(\text{CH}_3)_3\text{C}$; $n = 1-4$) and $((\text{C}_6\text{H}_5\text{O})_3\text{P})_2(\text{t-BuNC})\text{Mn}_2(\text{CO})_7$ by UV irradiation or by a thermal reaction in refluxing toluene.



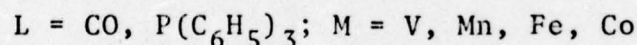
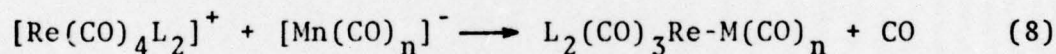
In view of this limited research, we decided to investigate the reactions of $\text{Mn}_2(\text{CO})_{10}$ with phenyl isocyanide and, more importantly, to investigate the possibility of synthesizing zero valent manganese isocyanide complexes of higher substitution than those currently known. Our reaction of $\text{Mn}_2(\text{CO})_{10}$ with $\text{C}_6\text{H}_5\text{NC}$ in refluxing THF resulted in the isolation of only mono- and disubstituted complexes. We therefore, turned to a different synthetic approach, namely the nucleophilic attack on isocyanide complexes of manganese(I) by reaction with manganese pentacarbonyl anion, $\text{Mn}(\text{CO})_5^-$. We had previously noted that the halide on complexes of the type $\text{Mn}(\text{CO})_{5-x}(\text{L})_x\text{X}$ ($\text{L} = \text{isocyanide}$; $\text{X} = \text{Br}, \text{Cl}$) could easily be removed by reaction with AgPF_6 (Chapter II & III) or exchanged as in reactions with NaCN (Chapter VI). We therefore felt that the $\text{Mn}(\text{CO})_5^-$ anion was nucleophilic enough to displace the halide on these complexes to form dimers of the type $\text{Mn}(\text{CO})_{5-x}(\text{L})_x\text{Mn}(\text{CO})_5$.



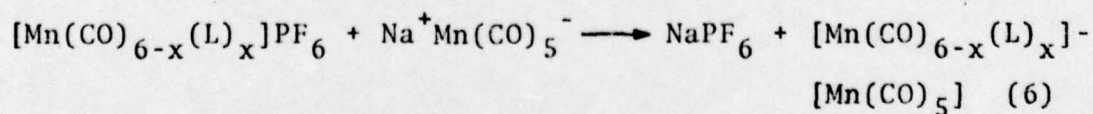
A recent review by King⁶ delineated the application of metal carbonyl anions in the synthesis of novel organometallic complexes. By reaction of various metal carbonyl anions with various alkyl halides he established a series of relative nucleophilicities of the anions as follows:

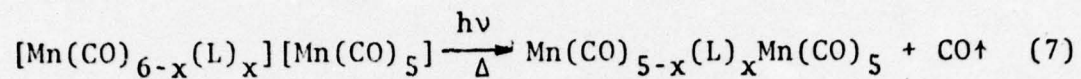


Research by Kruck and co-workers⁵ has shown that rhenium(I) carbonyl complexes of the type $[\text{Re(CO)}_4\text{L}_2]^+$ ($\text{L} = \text{CO}, \text{P}(\text{C}_6\text{H}_5)_3$) can react with a variety of metal carbonyl anions in the following manner:



In view of this, we also decided to investigate reactions of Mn(CO)_5^- with complexes of the type $\text{Mn(CO)}_{6-x}(\text{L})_x^+$ ($\text{L} = \text{isocyanide}$) and subsequently to investigate the possibility of removing a ligand from the resultant complex.





We further sought to characterize the expected products by infrared and mass spectral examination to determine any unique features of these zero-valent complexes.

B. RESULTS AND DISCUSSION

We approached the synthesis of these polynuclear metal carbonyl isocyanide complexes from a variety of directions. Since no researchers had attempted the direct reaction of $\text{Mn}_2(\text{CO})_{10}$ with aryl isocyanides (JPS¹ obtained $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})_2$ and $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$ by indirect means), we decided to use that simple approach first. It soon became apparent, however, that reaction in refluxing THF would yield only products of low substitution. In addition, contamination with free isocyanide made recovery of pure products difficult. Only the monosubstituted species, $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$, which was the major product, was obtained as a pure crystalline material. Its solubility in hydrocarbon solvents and tendency to darken on standing more closely approximate the characteristics of $\text{Mn}_2(\text{CO})_{10}$ than does the disubstituted complex, $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$, which was obtained in low yield as the only other product from the substitution reaction.

The infrared spectrum of the monosubstituted product was taken in CCl_4 in order to accurately compare it to the CCl_4 solution spectra of the complex prepared by JPS¹. As can be clearly seen from the tabulated absorptions (Table 1, Fig. 1), not only the number of peaks, but also the relative intensities of the peaks are decidedly different

for the two monosubstituted species reported. Added to this, the melting points are different enough (54° for the JPS species, 63° for the species in this work) and the analyses accurate enough to eliminate the possibility of impurities. This leads to the logical conclusion that two isomers have been prepared, one in which the phenyl isocyanide is bonded in the axial position (along the Mn-Mn line) and the other in which the ligand is bound equatorially. Unfortunately, infrared spectra of $\text{Mn}_2(\text{CO})_9\text{L}$ species tend to be ever more complicated than expected. A simplified approach toward the prediction of the number of carbonyl absorptions expected in a dinuclear manganese carbonyl-ligand complex is to treat each metal-ligand fragment separately. For example, the complex $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$, presuming an axially bound isocyanide, can be considered as a combination of a $\text{M}(\text{CO})_5\text{L}$ fragment and a trans- $\text{M}(\text{CO})_4\text{L}_2$ fragment. Using the Cotton, Kraihanzel¹⁶ model for complexes of the type $\text{M}(\text{CO})_{6-x}\text{L}_x$, the $\text{M}(\text{CO})_5\text{L}$ fragment would be expected to show three infrared active modes (2 A_1 's and an E_1) while the trans- $\text{M}(\text{CO})_4\text{L}_2$ fragment should show one infrared active mode (E_μ) for a combined total of 4 carbonyl absorptions. If the ligand is equatorially bound, the same type of qualitative approach yields 7 infrared active modes. It should be noted, however, that the infrared spectrum of the com-

plex, $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$, prepared by us fits neither of these approaches and this method should therefore be treated only as a rough approximation. Also, a monosubstituted complex, $\text{Mn}_2(\text{CO})_9(\text{CH}_3\text{NC})$, prepared by Manning, Newman and Grant⁴ (Table 1) has been shown to exhibit 8 carbonyl and 2 isocyanide absorptions which again does not fit the qualitative approach. In this instance, however, a good case can be made for the existence of structural isomers to further complicate the spectrum.

In comparing the spectrum of our disubstituted species, $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$, with that of the disubstituted species prepared by JPS (Table 1), a case can be made that the two are identical. The number of infrared absorptions and the relative intensities are identical, and within experimental error the absorption frequencies also agree. A paper by Manning, Lewis and Miller⁷ presented a detailed analysis of vibrational spectra of molecules of the type, $\text{Mn}_2(\text{CO})_8(\text{PR}_3)_2$, where the phosphine groups occupy the axial positions. Discounting the phosphines produces idealized D_{4d} symmetry for the molecules which then would have only a b_2 and a e_1 mode allowed in the infrared. The molecules prepared do show a strong e_1 absorption and concentrated solutions were shown to exhibit many more absorptions of lesser intensity. The point to be made, however, is that

the disubstituted phenyl isocyanide complex shows an absorption pattern indicative of a lower symmetry group than D_{4d} probably indicating the ligands are not both axially bound. Whether this complex pattern stems from possible asymmetry of the aryl isocyanide ligand, coupling of carbonyl and isocyanide vibrational modes, the existence of structural isomers or other factors is at this point indeterminable.

Another approach to the synthesis of these complexes has been the use of ultraviolet radiation to labilize the carbonyls. This approach has been successful in producing tetrasubstituted species at best but in all probability the identification of products by infrared becomes even more difficult due to the random labilization of carbonyls and formation of isomeric mixtures.

The direct substitution of isocyanides for carbonyls was a notably disappointing approach due to the limited substitution possible and the lack of control over the stereochemistry of the products. We therefore approached the synthesis of dinuclear manganese isocyanide complexes by nucleophilic attack of complexes of the type $Mn(CO)_{5-x}^-(RNC)_xX$ (R = aryl or alkyl isocyanide; X = Cl, Br) with $Mn(CO)_5^-$. The anion $Mn(CO)_5^-$ was easily prepared by reaction of Na/Hg amalgam with $Mn_2(CO)_{10}$.⁸ Recently, however, we have found it more efficient and cleaner to prepare the

anion by reaction of $\text{Mn}_2(\text{CO})_{10}$ with Na solvated by liquid ammonia.⁹ The reaction of $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$ with $\text{Na}^+\text{Mn}(\text{CO})_5^-$

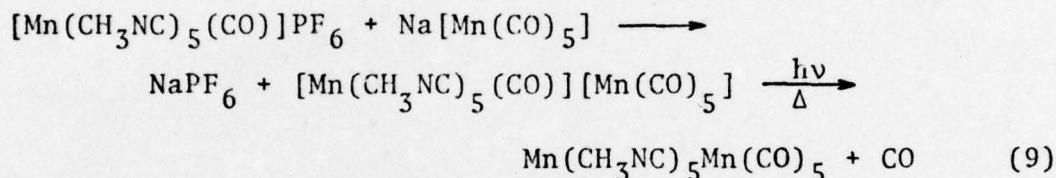
$$\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br} + \text{Na}^+\text{Mn}(\text{CO})_5^- \longrightarrow \text{NaBr} + \text{Mn}_2(\text{CH}_3\text{NC})_4(\text{CO})_6 \quad (8)$$

proved to be by far the least complicated among the syntheses attempted. The anion was prepared in THF and a THF solution of isocyanide complex was added. The $\text{Mn}(\text{CO})_5^-$ anion has a relatively long lifetime even when slowly exposed to air so the reaction could be monitored by taking routine infrared spectra of the reaction solvent and observing the gradual disappearance of the $\text{Mn}(\text{CO})_5^-$ $\nu(\text{CO})$ peaks ($1898, 1863 \text{ cm}^{-1}$). Once formed, the dinuclear product is air stable and easily recovered. A high resolution infrared spectrum of the product reveals the specificity of the reaction. The $\text{Mn}(\text{CO})_5$ fragment replaces the bromide ion resulting in a dinuclear complex in which the four isocyanide ligands produce a single $\nu(\text{CN})$ absorption (1955 cm^{-1} , Table 1, Fig. 1), a phenomenon which could only occur if all the isocyanides occupy equatorial positions. Another interesting observation that can be made concerns the marked similarity in frequencies of absorption of the $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})$ fragment ($\nu(\text{CN}) = 2155 \text{ cm}^{-1}$, $\nu(\text{CO}) = 1881 \text{ cm}^{-1}$) vs $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$ ¹⁰ ($\nu(\text{CN}) = 2142 \text{ cm}^{-1}$, $\nu(\text{CO}) = 1882 \text{ cm}^{-1}$). The presumption is made that the lowest energy $\nu(\text{CO})$ absorption can be assigned to the carbonyl on the manganese with iso-

cyanides, probably a valid presumption in view of the recognized poorer back bonding ability of CH_3NC vs CO . The $\text{Mn}(\text{CO})_5$ fragment therefore appears to exhibit an electron withdrawal effect similar to a halide ion. This phenomenon is also significant in that there appears to be little or no interaction or distortion due to coupling of $\nu(\text{CN})$ with $\nu(\text{CO})$. The preparation of dinuclear manganese carbonyl aryl-isocyanide complexes by reaction of $\text{Mn}(\text{p-ClC}_6\text{H}_5\text{NC})_5\text{Cl}$ and $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Cl}$ with $\text{Na}^+\text{Mn}(\text{CO})_5^-$ also proceeded smoothly at room temperature and was again monitored by observing the disappearance of the $\text{Mn}(\text{CO})_5^-$ $\nu(\text{CO})$ absorptions as before. The products $(\text{Mn}_2(\text{CO})_5(\text{p-ClC}_6\text{H}_5\text{NC})_5$ and $\text{Mn}_2(\text{CO})_6(\text{p-CH}_3\text{C}_6\text{H}_5\text{NC})_4$), however, proved to be almost impossible to recover in pure crystalline form and all attempts to grow reasonable crystals resulted in eventual decomposition even under the most controlled conditions. The infrared spectra of these aryl isocyanide complexes (Table 1) turned out to be somewhat more difficult to even rationalize qualitatively. The best that can be said is that there appears to be distinct absorption regions for $\nu(\text{CN})$ and $\nu(\text{CO})$ and the complexity of the patterns supports the existence of the dimetallic species.

It is by now well documented¹ that an alkyl isocyanide complex of the type MnL_5X corresponding to the known

Mn(aryl isocyanide)₅Cl has not been prepared. Therefore, an attempt to prepare a dinuclear complex of the type MnL₅Mn(CO)₅ (L = methyl isocyanide) had to be approached by a different synthetic route. We therefore applied the previously mentioned method of Kruck, Höfler and Noack⁵ and reacted the known complex [Mn(CH₃NC)₅(CO)]⁺ with Mn(CO)₅⁻ and then hoped to drive off the CO on the cation fragment.



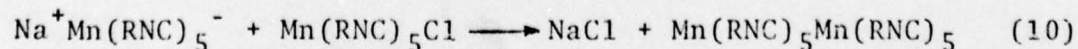
The first step of the reaction proceeded without complications and the complex [Mn(CH₃NC)₅(CO)][Mn(CO)₅] could be isolated as a white powder. The infrared spectrum (Table 1, Fig. 1) shows that both fragments of the complex maintain their individual previously known frequency and intensity patterns. We therefore rationalized that the carbonyl on the cation fragment, being least tightly bound, could be expected to be removed. However, all attempts including prolonged dry heating under vacuum at elevated temperatures (a procedure used successfully by Kruck⁵ to prepare ReCo(CO)₉ from [Re(CO)₆][Co(CO)₄]) and extended periods of ultraviolet irradiation of the solid under vacuum soon convinced us of the amazing stability of this complex.

We obtained mass spectral analyses on the complexes $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$, $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$, and $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{NC})_4$ (Tables 2,3, and 4; Figs. 2,3). Unfortunately, mass spectra of the higher substituted aryl isocyanide complexes could not be obtained due to the high molecular weights and low volatilities. Several points become quickly apparent in analyzing the mass spectra obtained. All the complexes exhibit parent ions, although they occur in low relative abundance. The complexes appear to lose carbonyls stepwise after ionization although all three species show a large gap between the parent and the next lower fragment. Winter and Kiser¹¹ have previously shown that binuclear carbonyls of cobalt and manganese decompose by successive loss of CO to form Co_2^+ and Mn_2^+ and may also break into mononuclear species at any time, one charged and one neutral. Lewis and Johnson¹² have found the cleavage of the metal cluster is dependent upon the metal and this tendency decreases rapidly in going from $\text{Mn}_2(\text{CO})_{10}$ to $\text{Re}_2(\text{CO})_{10}$. This is confirmed in our studies by the relative abundance of the fragments Mn_2^+ (~10) vs Mn^+ (100). McCleverty¹³ reported on the mass spectra of complexes of the type $\text{M}(\text{CO})_{6-x}(\text{RNC})_x$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$; $\text{R} = \text{alkyl or aryl}$) and also noted sequential loss of carbonyls to leave fragments of the type $\text{M}(\text{RNC})_x^+$. We note the same occurrence in the case

of the dinuclear manganese species. Thus species of the type $\text{Mn}_2(\text{RNC})_x^+$ and $\text{Mn}(\text{RNC})_x^+$ are present in high abundance. This can be rationalized by noting that the ion formed by loss of carbonyl is more stabilized than the ion formed by loss of isocyanide. This appears to be the result of delocalization of the positive charge through the $-\text{N}\equiv\text{C}$ bond. We further report high abundances of fragments of the type $\text{Mn}_2(\text{CN})_x^+$ and $\text{Mn}(\text{CN})_x^+$ indicative of the importance of α -cleavage in the fragmentation of isocyanides, a phenomenon which had also been previously noted.^{3,15} We further note the presence of an m/e peak of 93 as a fragment in the decomposition of the complexes $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$ and $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$ and have tentatively assigned this value to the fragment $\text{Mn}(\text{C})(\text{CN})^+$. It had been previously noted¹² that relatively high abundance of ions of the type $[\text{Re}(\text{CO})_x\text{C}]^+$ and $[\text{MnRe}(\text{CO})_x\text{C}]^+$ were a feature of the spectra of $\text{Re}_2(\text{CO})_{10}$ and $\text{MnRe}(\text{CO})_{10}$. We make particular note of the presence of species of the type $\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2^+$ in the spectrum of $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{NC})_4$ and $\text{Mn}(\text{CO})(\text{C}_6\text{H}_5\text{NC})_2^+$ in the spectrum of $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$ in relatively high abundances (17 and 11 respectively). This appears to be the result of rearrangement of the ligands due to the high temperatures involved, a fact not surprising in light of the fluxional behavior of $\text{Mn}_2(\text{CO})_7(\text{CH}_3\text{NC})_3$ seen by Adams.²

Finally, we noted the presence of significant abundances of species which appear to be the result of protonation of the isocyanide at the nitrogen. This is much more prevalent in the spectra of the dinuclear aryl isocyanide complexes where more hydrogen is available due to the fragmentation of the aryl ring. Thus species of the type $\text{Mn}(\text{C}_6\text{H}_5\text{NHC})^+$, $\text{Mn}(\text{C}_6\text{H}_5\text{NC})(\text{C}_6\text{H}_5\text{NHC})^+$ and $\text{C}_6\text{H}_5\text{NHC}^+$ are evident in the mass spectra of $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$ and $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$.

In conclusion, we offer some food for thought for future synthetic approaches to the preparation of dinuclear manganese carbonyl complexes of even higher ligand substitution. Adams¹⁴ has recently reported the successful preparation of methyl isocyanide derivatives of the manganese pentacarbonyl anion, $\text{Mn}(\text{CO})_{5-x}(\text{CNCH}_3)_x^-$ ($x = 1-3$) by reaction of the halide with Na/Hg amalgam. It is known that metal-alkyl isocyanide complexes are more electron rich than the corresponding aryl isocyanide complex.^{10,13} Therefore, although Adams reached a limit with the complex anion $\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_3^-$, the better π -acceptor aryl isocyanide ligands might well allow the preparation of the anions $\text{Mn}(\text{RNC})_4(\text{CO})^-$ and $\text{Mn}(\text{RNC})_5^-$ ($\text{R} = \text{aryl groups}$). Then one can envision reactions of the type



where R groups could be alike or different. Fluxional behavior studies, electrochemical investigations, and mass spectra would then no doubt prove to be very interesting.

C. EXPERIMENTAL

All reactions were run in a nitrogen atmosphere. Melting points, routine infrared spectra, and elemental analyses were obtained as reported in previous chapters. Infrared spectra for $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{NC})_4$ and $\text{Mn}_2(\text{CO})_5(\text{p-ClC}_6\text{H}_4\text{NC})_5$ were obtained at high resolution ($\pm 1 \text{ cm}^{-1}$) in the range 2200-1800 cm^{-1} on dichloromethane solutions using a Digilab FTS-20 spectrometer. Molecular weights were determined from mass spectral data, obtained on a AEI-902 mass spectrometer.

Dimanganese decacarbonyl, $\text{Mn}_2(\text{CO})_{10}$, was available in the laboratory. Sodium-mercury amalgam (0.75% Na) was prepared by slow addition of fine Na slivers to 100 g. Hg. Phenyl isocyanide was prepared as reported in previous chapters. Chloro pentakis (p-chlorophenyl isocyanide) manganese(I), $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$, bromocarbonyl tetrakis (methyl isocyanide) manganese(I), $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$, carbonyl pentakis (methyl isocyanide) manganese(I) bromide, $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})]\text{Br}$, and chlorocarbonyl tetrakis (p-tolyl isocyanide) manganese(I), $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$, were prepared as described in Chapter VI or reference 1.

Reaction of $\text{Mn}_2(\text{CO})_{10}$ with $\text{C}_6\text{H}_5\text{NC}$.

To a solution of $\text{Mn}_2(\text{CO})_{10}$ (7.8 g, 20 mmol) in 100 ml THF was added $\text{C}_6\text{H}_5\text{NC}$ (6.6 g, 64 mmol). The solution was refluxed for 4 h, then stirred at rt and monitored by infra-

red spectra until no further change could be observed (~12 h). The solvent was evaporated leaving a dark oil which was redissolved in CH_2Cl_2 . Addition of hexane resulted in precipitation of several grams of $\text{Mn}_2(\text{CO})_{10}$ which were filtered off. The solution was again evaporated, dissolved in a minimum amount of hexane, and placed on an alumina column, eluting three major bands with hexane. The first band contained more $\text{Mn}_2(\text{CO})_{10}$. The second band yielded 2.3 g of dark yellow crystals which melt at 63°C . The complex was presumed to be the monosubstituted $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$.

Anal. Calcd. for $\text{C}_{16}\text{H}_5\text{NO}_9\text{Mn}_2$: C, 41.34; H, 1.08; N, 3.01,

Found: C, 41.74; H, 1.14; N, 3.20.

Mass spec peak match. Calcd.: 464.87223

Found: 464.87259

The third band yielded 1.0 g of pale yellow crystals which were difficult to elute, only sparingly soluble in hexane, and tended to decompose in solution. The compound melts at $104 - 106^\circ \text{C}$. The complex was presumed to be the disubstituted $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$.

Mass spec peak match. Calcd.: 539.91975

Found: 539.91986

Preparation of $\text{Mn}_2(\text{CO})_6(\text{MeNC})_4$.

To a 250 ml three-necked flask fitted with an overhead stirrer and bottom release was added $\text{Mn}_2(\text{CO})_{10}$ (0.18 g, 0.46 mmole) in 100 ml THF. To this solution was added an excess of Na/Hg amalgam (0.75% - 10 g) and the reaction was stirred vigorously for 30 min. An infrared spectrum of the solution indicated complete conversion to $\text{Mn}(\text{CO})_5^-$. The unreacted Na/Hg amalgam was removed via the bottom release. To this solution of the anion was added $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Br}$ (0.30 g, 0.92 mmol) and the reaction was stirred at rt for 68 h. The solution was filtered under N_2 and the THF was removed. The residue was dissolved in CH_2Cl_2 and addition of hexane and cooling to -21°C resulted in the precipitation of yellow cubes in 49% yield. The compound decomposes without melting at $\sim 165^\circ\text{C}$.

Anal. Calcd. for $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_6\text{Mn}_2$: C, 38.00; H, 2.74; N, 12.67. Found: C, 37.00; H, 2.57; N, 12.00.

Mass spec peak match Calcd: 441.95164 Found: 441.95185

Preparation of $\text{Mn}_2(\text{CO})_5(\text{p-ClC}_6\text{H}_4\text{NC})_5$.

To a solution of $\text{Mn}_2(\text{CO})_{10}$ (0.25 g, 0.65 mmol) in 100 ml THF was added an excess of Na/Hg amalgam (20 g, 0.75% Na). The reaction was stirred with an overhead stirrer for 30 min. The unreacted Na/Hg amalgam was removed through a bottom release and $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ (1.0 g, 1.3 mmol) was

added to the solution and stirred at rt for 68 h. The solution was filtered, the solvent was removed, and the residue dissolved in a minimum of CH_2Cl_2 -hexane (1:1 ratio) and placed on an alumina column. One yellow band was eluted and the solvent evaporated leaving a yellow oil. The oil was dissolved in ethanol and careful addition of H_2O resulted in the precipitation of 0.40 g of yellow powder. The infrared spectrum (Table 1) and solubility properties are consistent with a possible $\text{Mn}_2\text{L}_5\text{L}'_5$ complex but all attempts to grow pure crystals resulted in eventual decomposition in solution.

Attempted Preparation of $\text{Mn}_2(\text{CH}_3\text{NC})_5(\text{CO})_5$.

To a solution of $\text{Mn}_2(\text{CO})_{10}$ (1.0 g, 2.6 mmol) in 100 ml THF was added Na/Hg amalgam (~20 g, 0.75% Na). The reaction was stirred at rt for 30 min and the excess amalgam removed. To the solution of $\text{Na}^+\text{Mn}(\text{CO})_5^-$ was added $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})]\text{Br}$ (2.0 g, 5.4 mmol) and the reaction was stirred at rt for 20 h. The solution was filtered under N_2 and the THF removed. The residue was heated under vacuum at 70-80 °C for 20 h and at 120 °C for an additional 20 h. Infrared spectra of the residue indicated no change from the original product. The pattern (Fig. 1) shows all the peaks for the known species $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})]^+$ and $\text{Mn}(\text{CO})_5^-$ and the compound melts >250 °C.

Reaction of $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ with $\text{Na}[\text{Mn}(\text{CO})_5]$.

To a solution of $\text{Na}[\text{Mn}(\text{CO})_5]$ (prepared from 0.20 g $\text{Mn}_2(\text{CO})_{10}$ and excess Na/Hg amalgam in the aforementioned manner) was added $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ (0.59 g, 1.0 mmol). The reaction was stirred at rt for 96 h, filtered under N_2 , and the solvent was removed. The remaining oil was dissolved in deaerated benzene and placed on an alumina column under N_2 . One yellow band was eluted and the solvent was evaporated. The residue was redissolved in CH_2Cl_2 -hexane, cooled to -78°C , and 0.25 g of yellow powder was recovered. All attempts at slow crystallization resulted in decomposition in solution but the infrared spectrum is consistent with a possible $\text{Mn}_2(\text{CO})_5(\text{L})_4(\text{CO})$ pattern (Table 1).

TABLE 1. INFRARED SPECTRAL DATA (cm^{-1})^a

Compound	$\nu_{\text{C}\equiv\text{N}}$	$\nu_{\text{C}\equiv\text{O}}$
$\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{NC})_4^{\text{b}}$	2155s	1996m, 1980m, 1958vs, 1924s, 1882s
$\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})^{\text{c}}$	2150m	2080s, 2010s, 1995vs 1980s, 1965vs
$\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2^{\text{c}}$	2150m, 2120s	2050s, 2010s, 1990vs 1950s
$\text{Mn}_2(\text{CO})_5(\text{p-C}_6\text{H}_4\text{NC})_5^{\text{b}}$	2147w, 2088s	2013m, 1987m(sh), 1970s, 1950m(sh), 1912m(sh)
$\text{Mn}_2(\text{CO})_6(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4$	2140w, 2090s	1980s, 1950s(sh), 1910m, 2040m
$[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})] -$ $[\text{Mn}(\text{CO})_5]$	2210w, 2150vs	1955m, 1900s, 1860vs
$\text{Mn}_2(\text{CH}_3\text{NC})(\text{CO})_9^{\text{d}}$	2169(sh) 2184vw	1962m, 1972m, 1982w, 1998vs, 2009m, 2028s, 2087(sh), 2090w
$\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})^{\text{d}}$	2169s, 2102s	2045s, 2016s, 1980s
$\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2^{\text{e}}$	2165w, 2128m	2061m, 2020m, 1996s 1957m

(a) IR spectra in CH_2Cl_2 solution taken on Beckman IR-10 spectrometer unless otherwise noted.

(b) High-resolution spectra ($\pm 1 \text{ cm}^{-1}$) in CH_2Cl_2 taken on Digilab FTS-20 spectrometer.

(c) IR spectra in CCl_4 taken on Beckman IR-10

(d) Ref. 4

(e) Ref. 1

TABLE 2. MASS SPECTROMETRIC FRAGMENTATION OF
 $\text{Mn}_2(\text{CH}_3\text{NC})_4(\text{CO})_6$

Major Peaks ^a	Species	Intensity
442	$\text{Mn}_2(\text{CH}_3\text{NC})_4(\text{CO})_6^+$	1
345	$\text{Mn}_2(\text{CH}_3\text{NC})_3(\text{CO})_4^+$	1
317	$\text{Mn}_2(\text{CH}_3\text{NC})_3(\text{CO})_3^+$	8
304	$\text{Mn}_2(\text{CH}_3\text{NC})_2(\text{CO})_4^+$	11
289	$\text{Mn}_2(\text{CH}_3\text{NC})_3(\text{CO})_2^+$	7
276	$\text{Mn}_2(\text{CH}_3\text{NC})_2(\text{CO})_3^+$	30
263	$\text{Mn}_2(\text{CH}_3\text{NC})(\text{CO})_4^+$	5
248	$\text{Mn}_2(\text{CH}_3\text{NC})_2(\text{CO})_2^+$	10
247	$\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})^+$	8
234	$\text{Mn}(\text{CH}_3\text{NC})_3(\text{CO})_2^+$	17
233	$\text{Mn}_2(\text{CH}_3\text{NC})_3^+$	20
220	$\text{Mn}_2(\text{CH}_3\text{NC})_2(\text{CO})^+$	9
192	$\text{Mn}_2(\text{CH}_3\text{NC})_2^+$	6
178	$\text{Mn}(\text{CH}_3\text{NC})_3^+$	53
165	$\text{Mn}(\text{CH}_3\text{NC})_2(\text{CO})^+$	8
163	$\text{Mn}(\text{CH}_3\text{NC})_2(\text{CN})^+$	10
151	$\text{Mn}_2(\text{CH}_3\text{NC})^+$	6
137	$\text{Mn}(\text{CH}_3\text{NC})_2^+$	75

TABLE 2. (Contd.)

Major Peaks ^a	Species	Intensity
136	$\text{Mn}_2(\text{CN})^+$	24
122	$\text{Mn}(\text{CH}_3\text{NC})(\text{CN})^+$	25
110	Mn_2^+	9
96	$\text{Mn}(\text{CH}_3\text{NC})^+$	100
81	$\text{Mn}(\text{CN})^+$	32
55	Mn^+	100

(a) All peaks with intensity >5 are included; M^+ and $\text{M}^+ - 97$ included to indicate gap between the parent ion and the next highest peak.

TABLE 3. MASS SPECTROMETRIC FRAGMENTATION OF
 $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$

Major Peaks ^a	Species	Intensity
465	$\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})^+$	2
353 ^b	$\text{Mn}_2(\text{CO})_5(\text{C}_6\text{H}_5\text{NC})^+$	3
325	$\text{Mn}_2(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})^+$	10
297	$\text{Mn}_2(\text{CO})_3(\text{C}_6\text{H}_5\text{NC})^+$	18
270	$\text{Mn}(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})^+$	23
269	$\text{Mn}_2(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})^+$	11
242	$\text{Mn}(\text{CO})_3(\text{C}_6\text{H}_5\text{NC})^+$	5
241	$\text{Mn}_2(\text{CO})(\text{C}_6\text{H}_5\text{NC})^+$	13
214	$\text{Mn}(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})^+$	9
213	$\text{Mn}_2(\text{C}_6\text{H}_5\text{NC})^+$	17
186	$\text{Mn}(\text{CO})(\text{C}_6\text{H}_5\text{NC})^+$	7
159	$\text{Mn}(\text{C}_6\text{H}_5\text{NHC})^+$	5
158	$\text{Mn}(\text{C}_6\text{H}_5\text{NC})^+$	51
110	Mn_2^+	19
104	$\text{C}_6\text{H}_5\text{NHC}^+$	4
103	$\text{C}_6\text{H}_5\text{NC}^+$	33
93	$\text{Mn}(\text{C})(\text{CN})^+$	10
78	C_6H_6^+	7

TABLE 3. (Contd.)

Major peaks ^a	Species	Intensity
77	C_6H_5^+	7
76	C_6H_4^+	18
55	Mn^+	100

(a) All peaks with intensity > 5.

(b) First peak below parent M^+ .

TABLE 4. MASS SPECTROMETRIC FRAGMENTATION OF
 $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$

Major Peaks ^a	Species	Intensity
540 ^b	$\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$	0.2
456 ^b	$\text{Mn}_2(\text{CO})_5(\text{C}_6\text{H}_5\text{NC})_2^+$	0.5
428 ^c	$\text{Mn}_2(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})_2^+$	2.5
400	$\text{Mn}_2(\text{CO})_3(\text{C}_6\text{H}_5\text{NC})_2^+$	5
372 ^c	$\text{Mn}_2(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})_2^+$	1.5
345	$\text{Mn}(\text{CO})_3(\text{C}_6\text{H}_5\text{NC})_2^+$	22
325	$\text{Mn}_2(\text{CO})_4(\text{C}_6\text{H}_5\text{NC})^+$	5
316	$\text{Mn}_2(\text{C}_6\text{H}_5\text{NC})_2^+$	9
297	$\text{Mn}_2(\text{CO})_3(\text{C}_6\text{H}_5\text{NC})^+$	5
289	$\text{Mn}(\text{CO})(\text{C}_6\text{H}_5\text{NC})_2^+$	11
262	$\text{Mn}(\text{C}_6\text{H}_5\text{NC})(\text{C}_6\text{H}_5\text{NHC})^+$	5
261	$\text{Mn}(\text{C}_6\text{H}_5\text{NC})_2^+$	30
213	$\text{Mn}_2(\text{C}_6\text{H}_5\text{NC})^+$	5
159	$\text{Mn}(\text{C}_6\text{H}_5\text{NHC})^+$	7
158	$\text{Mn}(\text{C}_6\text{H}_5\text{NC})^+$	59
110	Mn_2^+	11
104	$\text{C}_6\text{H}_5\text{NHC}^+$	10
103	$\text{C}_6\text{H}_5\text{NC}^+$	100
93	$\text{Mn}(\text{C})(\text{CN})^+$	32

TABLE 4. (Contd.)

Major Peaks ^a	Species	Intensity
81	$\text{Mn}(\text{CN})^+$	5
78	C_6H_6^+	7.5
77	C_6H_5^+	18
76	C_6H_4^+	55
75	C_6H_3^+	11
74	C_6H_2^+	7
55	Mn^+	87

- (a) All peaks with intensity > 5.
- (b) Parent (M^+) and ($\text{M}^+ - 84$) peak included to show separation between parent and first lower peak.
- (c) Included to show stepwise loss of carbonyl.

Figure 1
Infrared Spectra of Dimanganese
Carbonyl Isocyanide Complexes

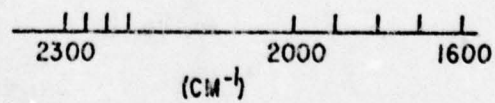
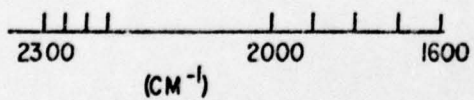
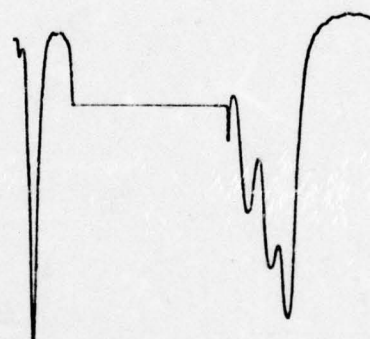
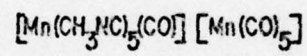
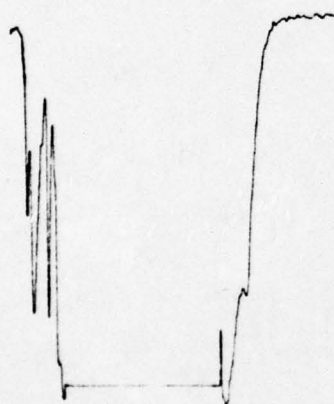
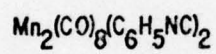
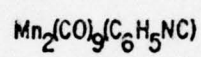
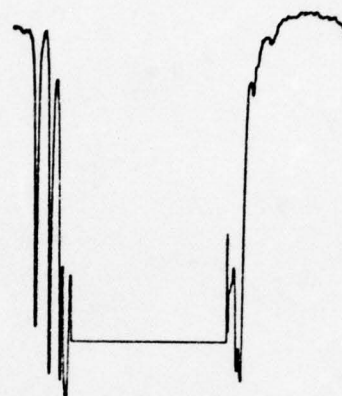
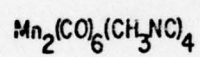
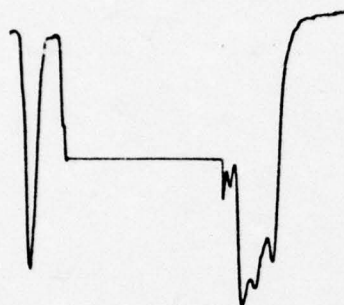


Figure 2

Mass Spectrum of $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$

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MS9

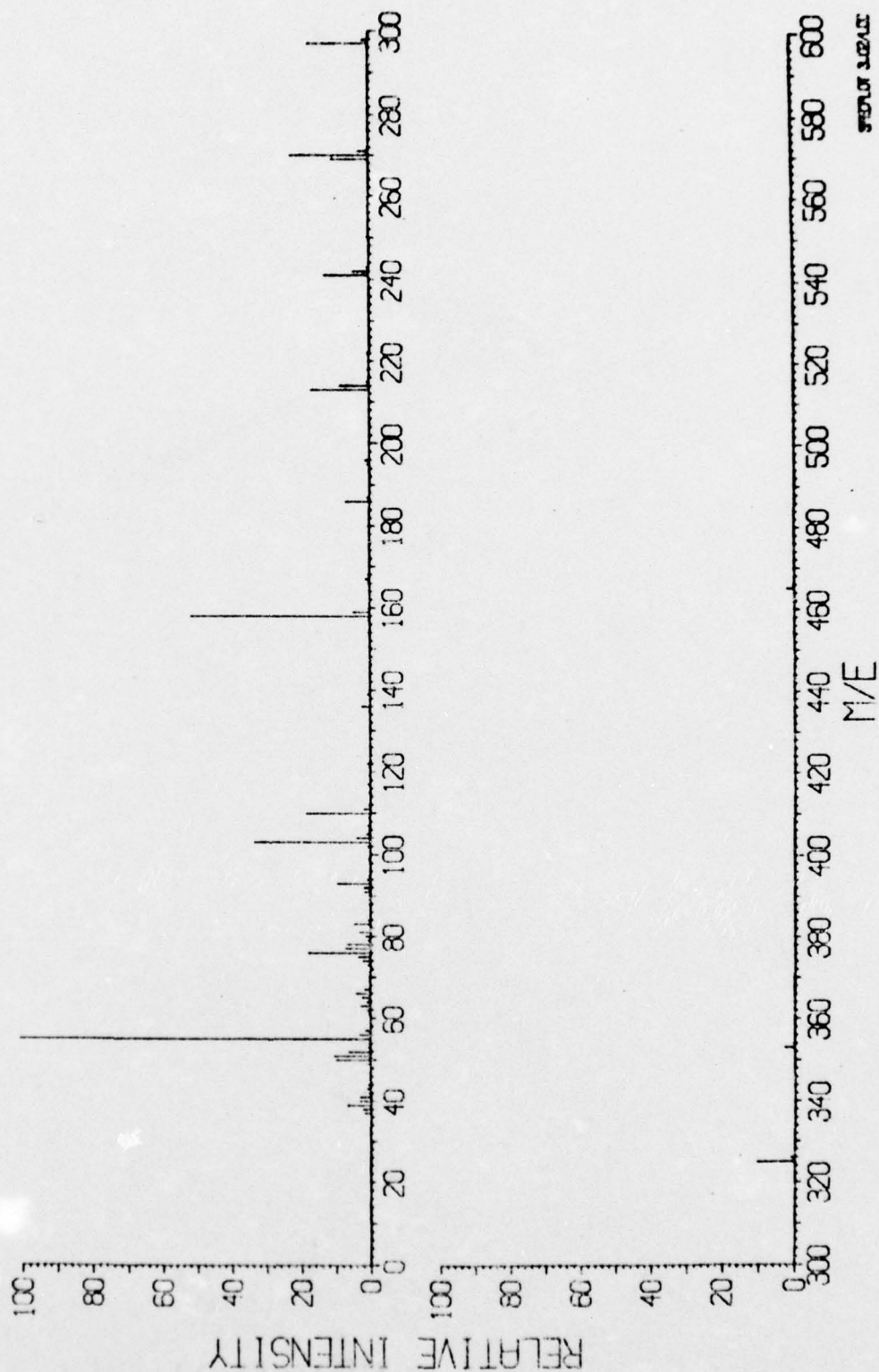
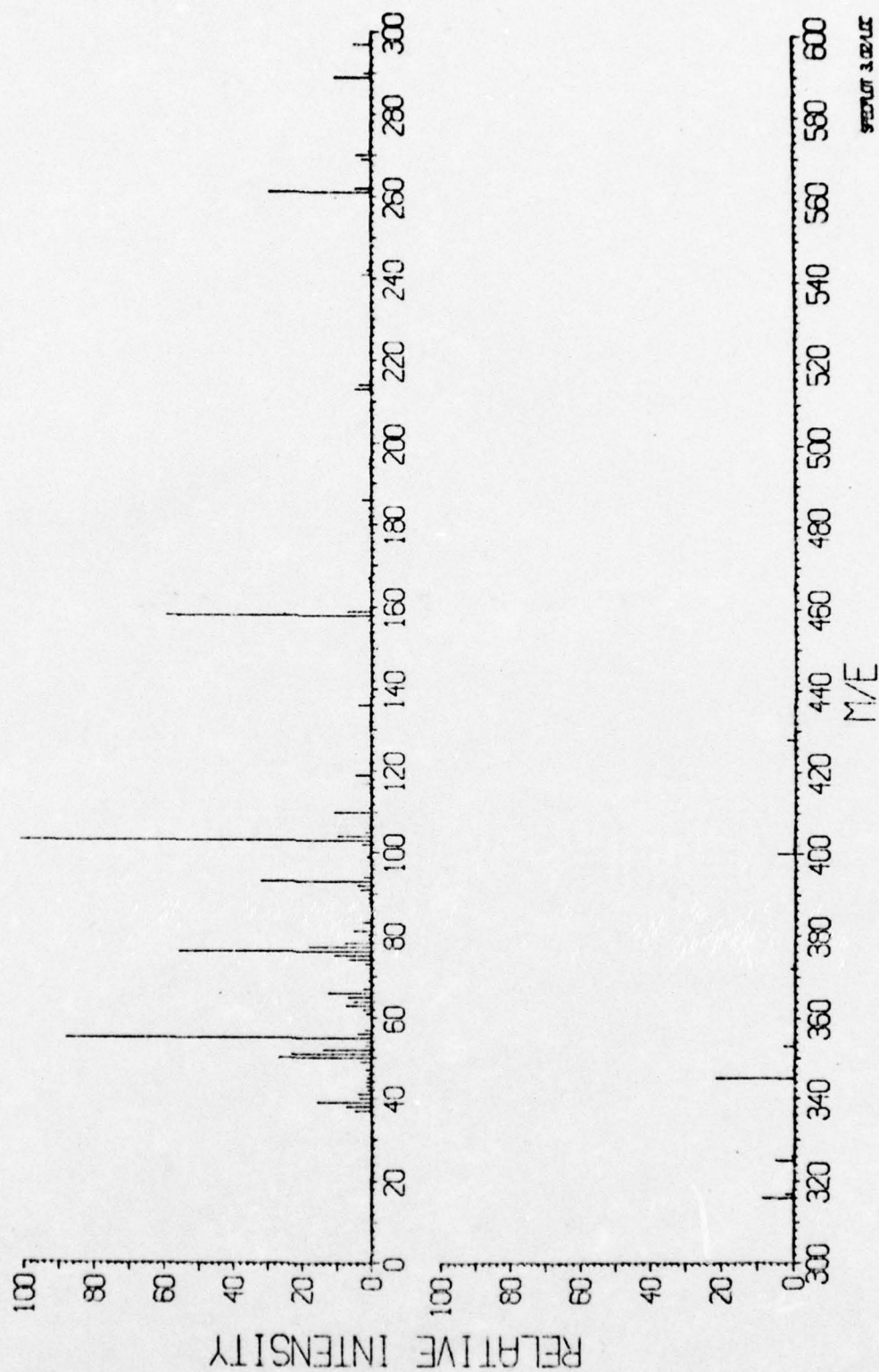


Figure 3

Mass Spectrum of $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$

UNIVERSITY OF WISCONSIN CHEMISTRY DEPARTMENT

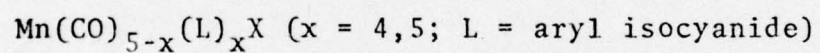
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CHAPTER VI

SYNTHESIS, CHARACTERIZATION AND ELECTROCHEMISTRY
OF MANGANESE(I) COMPLEXES OF THE TYPE

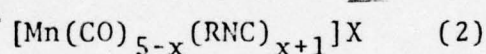
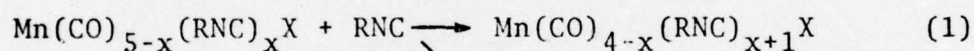
A. INTRODUCTION

Among the extensive research in the field of metal isocyanide complexes, four papers describe the reactions of $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{I}, \text{Br}, \text{Cl}$) with isocyanides.

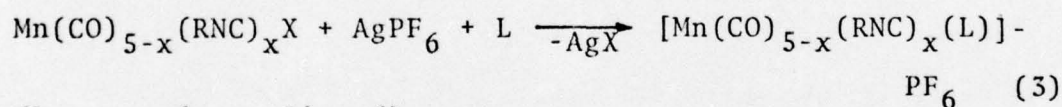
Hieber and Schropp¹ reported the synthesis of $\text{Mn}(\text{CO})_3(\text{CH}_3\text{OC}_6\text{H}_4\text{NC})_2\text{Cl}$ by reaction of $\text{Mn}(\text{CO})_5\text{Cl}$ with $p\text{-CH}_3\text{OC}_6\text{H}_4\text{NC}$ in ethanol at 70° . Angelici and Basolo² later reported the preparation of the complex $\text{Mn}(\text{CO})_4(\text{CNC}_2\text{H}_5)\text{Cl}$. A more detailed study by Joshi, Pauson and Stubbs³ covered the reactions of $\text{Mn}(\text{CO})_5\text{X}$ with phenyl isocyanide. They reported the formation of $\text{Mn}(\text{CO})_5(\text{C}_6\text{H}_5\text{NC})_2\text{Br}$ in refluxing ethanol, $\text{Mn}(\text{CO})_2(\text{C}_6\text{H}_5\text{NC})_3\text{Br}$ in diglyme at 100° , and more highly substituted species when the reactions were run in refluxing THF. More recently, Treichel and co-workers⁴ reinvestigated the reactions of $\text{Mn}(\text{CO})_5\text{X}$ with phenyl isocyanide and found significant differences from previously reported results.³ Specifically, reaction of $\text{Mn}(\text{CO})_5\text{Cl}$ with phenyl isocyanide in refluxing THF led to the formation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ and $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{Cl}$ while reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with phenyl isocyanide under the same conditions produced primarily $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Br}$.

A review by Abel and Tyfield⁵ summarizes reactions of systems of the type $\text{M}(\text{CO})_n\text{X}$ ($\text{M} = \text{Mn}, \text{CpMo}, \text{CpFe}, \text{etc.};$

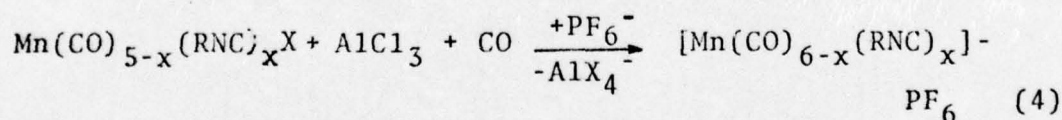
X = Br, Cl) with free ligands to form cationic metal carbonyls. These reactions can occur by direct ligand displacement of the halide or by assisted halide displacement using halide acceptors, thus indicating the synthetic utility of these halometalcarbonyl systems. Previous work in our group⁴ and previous chapters in this thesis have shown that this synthetic approach to cationic complexes can be extended to halometalisocyanide systems as well. Hence, reactions of the type



(R = alkyl, aryl; X = Br, Cl)



(L = any donor ligand)



are by now well documented.

In all of this previous research, the $\text{Mn}(\text{CO})_{6-x}(\text{RNC})_x\text{X}$ complexes have been prepared as precursors for the synthesis of cationic mixed ligand complexes. Minimal attention has been directed at the starting materials themselves, so we sought to obtain more information about

the properties of these precursors, directing particular attention to the halomanganesearylisocyanide complexes.

It has been shown^{4,6} on the basis of electrochemical studies of aryl vs alkyl isocyanide complexes that aryl isocyanides are better π -acceptors than alkyl isocyanides. Also, our work in Chapter I has shown the range of π -acceptor strengths of the aryl isocyanide ligand by showing the effect of substituent groups on the ring. With this in mind, it seems reasonable to expect differences in reactivities of these ligands when reacted with $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}$). To date, only the reactions of $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$) with phenyl isocyanide^{3,4} have been reported. We therefore decided to prepare a variety of complexes of the type $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x\text{X}$ ($x = 4, 5$; $\text{X} = \text{Cl}, \text{Br}$) for several reasons. First, we wanted to examine the possibility of variations in reactivity based on electron withdrawing or donating ring substituents on the aryl isocyanides. Second, we wanted to examine the electrochemical behavior of these complexes to determine the feasibility of chemically preparing $17 e^-$ species having some possible synthetic utility. Toward this end, we also decided to vary the X group by preparing $\text{Mn}(\text{CO})_{5-x}^-(\text{RNC})_x\text{X}$ complexes where $\text{X} = \text{Cl}, \text{Br}, \text{CN}$, and SnCl_3 and to

examine this effect electrochemically. The initial part of that work appeared in a preliminary communication.⁷ Finally, we decided to examine the $\nu(\text{CN})$ and $\nu(\text{CO})$ regions of the infrared spectrum in an attempt to correlate the frequencies observed with the electrochemical data, as we had previously done in Chapter II.

B. RESULTS AND DISCUSSION

It is known that reaction of $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with isocyanides yields several products, depending on the conditions employed.^{3,4} In this study we concentrated our efforts on the preparation of the higher substituted $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x\text{X}$ ($\text{R} = \text{aryl isocyanide}; \text{X} = \text{Cl}, \text{Br}; x = 4, 5$) complexes. The choice of halide ($\text{Mn}(\text{CO})_5\text{Cl}$ vs $\text{Mn}(\text{CO})_5\text{Br}$) therefore becomes more crucial to the synthesis. The differences in reactivity of the two halopentacarbonyls have been quantitatively investigated by Basolo and coworkers, who found that both for carbonyl exchange⁸ and for reaction with a variety of other ligands,² the rates fall in the order $\text{Cl} > \text{Br} > \text{I}$. These results can be rationalized in terms of the difference in electronegativities of the halide. The less electronegative bromine allows more effective back donation to the CO, thus leading to stronger metal-carbon bonding. With this in mind, we reacted a number of aryl isocyanides having electron withdrawing and donating groups in the para position with both $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_5\text{Br}$. The reactions were run in refluxing THF; reaction times were maintained between 6-7 hours. The products were identified by their characteristic $\nu(\text{CN})$ and $\nu(\text{CO})$ absorptions combined with

the expected yellow to orange colors expected of neutral $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x\text{X}$ complexes. The colors are particularly useful in distinguishing between the white or pale yellow MnL_6^+ complexes, which are also formed in these reaction and the yellow-orange to deep red MnL_5X complexes. These complexes are often difficult to identify by infrared alone since the strong T_{1u} absorption mode of the MnL_6^+ complex ($\sim 2070\text{ cm}^{-1}$) can overlap and obscure the strong E_1 mode of the MnL_5X complex ($\sim 2050\text{ cm}^{-1}$). The $\text{Mn}(\text{RNC})_4(\text{CO})\text{X}$ complexes are the easiest to identify by infrared since they all exhibit a single strong $\nu(\text{CN})$ absorption (E mode, $\approx 2090\text{ cm}^{-1}$) and a single $\nu(\text{CO})$ absorption (A_1 mode, $1900\text{--}2000\text{ cm}^{-1}$).

The results of the reactions allowed us to make a few generalities. First, in contrast to previously reported results,^{3,4} we successfully prepared MnL_5X complexes from both $\text{Mn}(\text{CO})_5\text{Cl}$ and $\text{Mn}(\text{CO})_5\text{Br}$. However, as expected on the basis of reactivity differences, reaction of an aryl isocyanide with $\text{Mn}(\text{CO})_5\text{Cl}$ produced a higher percentage yield of the MnL_5X complex (relative to $\text{MnL}_4(\text{CO})\text{X}$) than reaction of the same isocyanide with $\text{Mn}(\text{CO})_5\text{Br}$ under the same conditions. Second, we found that $\text{Mn}(\text{RNC})\text{Br}$ complexes in which the aryl isocyanide has strong electron withdrawing groups on the ring are the easiest to

isolate, exhibit the greatest stability against loss of ligand, and are consistently obtained in the highest yield. Dirreen⁹ had previously reacted $\text{Mn}(\text{CO})_5\text{Br}$ with a strongly electron withdrawing pentachlorophenyl isocyanide $\text{C}_6\text{Cl}_5\text{NC}$, producing the first reported example of an $\text{Mn}(\text{RNC})_5\text{Br}$ complex. In this work we successfully prepared the complex $\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5\text{Br}$ and note its high thermal and kinetic stability. Further, we have been notably unsuccessful in isolating even the $\text{Mn}(\text{RNC})_5\text{Cl}$ complex when R is the strongly donating $\text{p-CH}_3\text{O}$ group. We also note the properties of the complex $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{Br}$. The complex was difficult to isolate; repeated crystallization attempts from CH_2Cl_2 -hexane resulted in the recovery of small amounts of $[\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_6]\text{Br}$ indicating a certain degree of ligand dissociation and further reaction. Also, even after isolation of apparently pure $\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_5\text{Br}$, the material tends to collapse into an amorphous mass emitting a strong, constant odor of isocyanide. These variations in properties can again be rationalized in terms of the differing degree of π -acceptor strength among the aryl isocyanides. A strongly electron withdrawing isocyanide ($\text{p-NO}_2\text{C}_6\text{H}_4\text{NC}$, $\text{p-ClC}_6\text{H}_4\text{NC}$, $\text{C}_6\text{Cl}_5\text{NC}$) by accepting a larger share of the electron donation from

the metal than an aryl isocyanide with a donor substituent, allows the formation of stronger M-C bonds with the isocyanide thus stabilizing the complex against ligand loss. In addition, using the same argument as that employed to explain the reactivity differences in the series $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Br}, \text{Cl}, \text{I}$), stepwise substitution of carbonyls by good π -acceptors does not strengthen the remaining metal-carbonyl M-C bond to the extent a poorer π -acceptor would. Accurate quantitative support for this subtle difference in reactivity is difficult to obtain, however, especially if based purely on relative yields of higher substituted products. Differences in ease of workup, kinetic differences, and varying extent of side reaction interference can all combine to produce less than linear correlation of product yields with ring substituent type according to the previous qualitative argument.

Isolation of the complex $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}$ deserves some special mention. The complex was recovered by fractional crystallization of a mixture of products obtained from the reaction of $\text{Mn}(\text{CO})_5\text{Br}$ with $\text{C}_6\text{H}_5\text{NC}$ several years earlier. The crude mixture was initially presumed to consist of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CO})]\text{Br}$ and $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Br}$. It can be postulated that the carbonyl of the $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5(\text{CO})]\text{Br}$ might have been photolytically removed by long term exposure to

sunlight. However, in view of the fact that MnL_5Br complexes have been prepared even when $\text{L} = \text{p-CH}_3\text{C}_6\text{H}_4\text{NC}$, it seems more likely that the complex $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}$ was indeed formed but its presence not noticed in the original reaction.

The complexes $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{SnCl}_3$ and $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{SnCl}_3$ were prepared by stirring solutions of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})\text{Cl}$ and $\text{Mn}(\text{C}_6\text{H}_5\text{NC})(\text{CO})\text{Cl}$ with $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. The $-\text{SnCl}_3$ groups appear to add considerable stabilization to the complexes by withdrawing a significant amount of electron density from the electron-rich metal center. This is supported by the electrochemical measurements (Table 2) which show a sizable increase in oxidation potential between the complexes $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ (0.29 v) and $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{SnCl}_3$ (0.86 v) and also between the complexes $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Br}$ (0.76 v) and $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{SnCl}_3$ (1.18 v). In the latter case it should also be noted that the carbonyl absorption frequency, $\nu(\text{CO})$, shows a sizable shift (1905 cm^{-1} to 1965 cm^{-1} , Table 1), which would be expected in view of the reduced electron density available for the metal to donate to the π^* orbital of the carbonyl. It is also interesting to compare the difference in $E_{1/2}$ values between the two MnL_5X species (0.57 v) vs the difference between the Mn-

$L_4(CO)X$ species (0.42 v). The smaller difference in the latter case might well be rationalized on the basis of the greater flexibility of the carbonyl ligand as a π -acceptor.

The complex $Mn(C_6H_5NC)_5CN$ was formed by stirring $Mn-(C_6H_5NC)_5Br$ with NaCN. The exchange was facile and the product easily isolated. The oxidation potential (0.66 v, Table 2) is again consistent with the stronger electron withdrawing ability of the -CN group compared with halides. The complex was impossible to identify by infrared because the pattern is identical to that of the starting material, $Mn(C_6H_5NC)_5Br$, and the cyanide stretch is not observed presumably being very weak.

Among the series of complexes, $Mn(RNC)_5X$ (R = substituted aryl isocyanides; X = Cl, Br), the electrochemical measurements again show the expected changes in oxidation potentials as the substituent group is varied between σ donor and σ withdrawer (See Chapter I). Therefore, it can be seen from Table 2 that $E_{1/2}$ values decrease as expected in the order $Mn(p-NO_2C_6H_4NC)_5Br > Mn(p-ClC_6H_4NC)_5Cl > Mn(C_6H_5NC)_5Br > Mn(p-CH_3C_6H_4NC)_5Br$. The complex $Mn(m-CF_3C_6H_4NC)_4(CO)Cl$ also exhibits the effect of the electron withdrawing m- CF_3 group when compared electrochemically to $Mn(C_6H_5NC)_4(CO)Br$ (0.96 v vs 0.76 v). This is again reflected in the shift in carbonyl absorption frequency (1920

cm^{-1} for $\text{Mn}(\text{m-CF}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ vs 1905 cm^{-1} for $\text{Mn}(\text{C}_6\text{H}_5\text{-NC})_4(\text{CO})\text{Br}$). It should be noted that the choice of Cl or Br as the X group produces only a small difference in the $E_{1/2}$ values (MnL_5Br is $\sim 0.03 \text{ v} > \text{MnL}_5\text{Cl}$) and thus is used for convenience in the comparisons.

It should again be noted that among the series of MnL_5X complexes, the changes in $E_{1/2}$ are not reflected in the changes in $\nu(\text{CN})$ which might be expected due to variable electron density available for donation to the π^* of the isocyanide carbon. The same effect was noted for the MnL_6^+ series discussed in Chapter I and the qualitative rationalization presented there applies here.

Finally, we might direct a few words toward future synthetic potential of these MnL_5X and $\text{MnL}_4(\text{CO})\text{X}$ complexes. A recent paper by Adams¹¹ presented evidence for the synthesis of a series of anions of the type $\text{Mn}(\text{CO})_{5-x}(\text{CNCH}_3)_x^-$ ($x = 1-3$) and discussed the value of the anions as reagents in the synthesis of isocyanide compounds of the type $\text{Mn}(\text{CO})_4^-(\text{CNCH}_3)\text{R}$. The synthesis of these anions from the corresponding halides, $\text{Mn}(\text{CO})_{5-x}(\text{CNCH}_3)_x\text{X}$, by reduction with sodium can obviously be extended to the aryl isocyanides. In fact, on the basis of the improved π -acceptor strength of the aryl isocyanides, more highly substituted anions can be expected. Aryl isocyanides have been shown to be much

more versatile ligands than carbonyls based on the possibility of altering the number and type of substituents on the ring. It is not unreasonable, therefore, to expect to find the right combination to form stable complexes of the type $\text{Mn}(\text{RNC})_5\text{R}$. The possibility of using these anions to form zero valent manganese complexes of the type $\text{Mn}_2(\text{CO})_{10-x}^-(\text{RNC})_x$ has been previously discussed (Chapter IV).

C. EXPERIMENTAL

All reactions were routinely run in a nitrogen atmosphere. Infrared spectra, melting points, electrochemical data and elemental analyses were obtained as described in previous chapters.

Bromopentacarbonyl manganese(I), $\text{Mn}(\text{CO})_5\text{Br}$, and chloropentacarbonyl manganese(I) were prepared as described by King¹⁰ by reaction of manganese decacarbonyl with the halogen. All isocyanides were prepared as mentioned in previous chapters. Sodium cyanide, NaCN , and tin dichloride dihydrate, $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, were used as purchased.

Tetrahydrofuran was purified by distillation from lithium aluminum hydride. All other solvents were analytical grade and used without further purification.

Preparation of $\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5\text{Br}$.

To a solution of $\text{Mn}(\text{CO})_5\text{Br}$ (0.22 g, 0.80 mmol) in 50 ml THF was added $\text{p-NO}_2\text{C}_6\text{H}_4\text{NC}$ (0.65 g, 4.4 mmol). The reaction was refluxed for 48 h, cooled, and 0.35 g of dark orange powder ($[\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5]\text{Br}$) was filtered off. The THF solution was dried and the residue redissolved in CH_2Cl_2 . Slow diffusion of diethyl ether into the red solution resulted in the formation of long flat needles having green reflectances. Filtration resulted in the recovery of 0.10 g

(14.3% yield) of $\text{Mn}(\text{p-NO}_2\text{C}_6\text{H}_4\text{NC})_5\text{Br}$. The compound decomposes without melting $> 300^\circ\text{C}$.

Anal. Calcd. for $\text{C}_{35}\text{H}_{20}\text{N}_{10}\text{O}_{10}\text{BrMn}$: C, 48.02; H, 2.30; N, 16.00.

Found: C, 46.98; H, 2.44; N, 14.95.

Preparation of $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$.

To a solution of $\text{Mn}(\text{CO})_5\text{Cl}$ (2.3 g, 10 mmol) in 100 ml THF was added $\text{p-ClC}_6\text{H}_4\text{NC}$ (8.2 g, 60 mmol). The reaction was refluxed for 7 h, cooled, and a pale yellow precipitate ($[\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_6]\text{Cl}$, 1.8 g, 20% yield) filtered off. The THF solution was dried, redissolved in CH_2Cl_2 , and 5.0 g of a mixture of $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ and $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ precipitated on addition of hexane. The mixture was redissolved in CHCl_3 and red needles of $\text{Mn}(\text{p-ClC}_6\text{H}_4\text{NC})_5\text{Cl}$ (2.5 g, 32% yield) were precipitated and recovered on addition of hexane. The compound decomposes without melting $> 150^\circ\text{C}$.

The following compounds were prepared by the same route by refluxing either $\text{Mn}(\text{CO})_5\text{Cl}$ or $\text{Mn}(\text{CO})_5\text{Br}$ with the appropriate isocyanide in THF.

$\text{Mn}(\text{p-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Br}$. Obtained as orange cubes from CH_2Cl_2 -hexane in 47% yield. The compound melts at $173\text{--}175^\circ\text{C}$ with decomposition.

Mn(p-CH₃C₆H₄NC)₅Br. Obtained as red-orange prisms from CHCl₃-heptane in 31% yield. The compound was identified by its infrared spectrum and tends to collapse into an amorphous semi-solid on standing.

Mn(p-CH₃C₆H₄NC)₅Cl. Obtained as yellow-orange needles from CHCl₃-heptane in 52% yield. The compound melts at 162-163 °C. with decomposition.

Mn(m-CF₃C₆H₄NC)₄(CO)Cl. Obtained as yellow powder from acetone-heptane in 22% yield. The compound melts at 150 °C. with decomposition.

Preparation of Mn(C₆H₅NC)₅CN.

To solution of Mn(C₆H₅NC)Br (0.50 g, 0.77 mmol) in 40 ml acetone was added NaCN (0.05 g, 1.0 mmol) in 10 ml H₂O. The solution was stirred at rt for 1 h, the acetone was evaporated, and the aqueous layer was shaken with benzene. The benzene layer was separated and dried with MgSO₄ and filtered. The benzene was removed and the residue dissolved in CH₂Cl₂. Addition of hexane resulted in the recovery of 0.25 g of pale yellow crystals in 54% yield. The compound darkens and decomposes at 170 °C.

Anal. Calcd. for C₃₆H₂₅N₆Mn: C, 72.48; H, 4.22; N, 14.09.

Found: C, 72.08; H, 4.38; N, 13.34.

Preparation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{SnCl}_3$.

To a solution of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ (0.60 g, 1.0 mmol) in 100 ml THF was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.40 g, 1.5 mmol). The reaction was stirred at rt for 2 h, the solvent was evaporated, and the residue redissolved in CHCl_3 and filtered. Addition of heptane to the filtrate produced yellow needles of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{SnCl}_3$ in 94% yield. The compound melts at 192-194 °C.

Anal. Calcd. for $\text{C}_{35}\text{H}_{25}\text{N}_5\text{Cl}_3\text{SnMn}$: C, 52.84; H, 3.17; N, 8.80.

Found: C, 51.60; H, 3.01; N, 8.65.

Preparation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{SnCl}_3$.

To a solution of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_4(\text{CO})\text{Cl}$ in 100 ml THF was added $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (0.40 g, 1.5 mmol). The reaction was stirred at rt for 12 h. The solvent was reduced under water aspirator pressure at rt until a small volume of liquid remained. The solution was shaken with CHCl_3 and the CHCl_3 layer was removed, dried with MgSO_4 , and filtered. Addition of heptane to the solution produced 0.70 g of yellow cubes in 97% yield. The compound melts at 159-161 °C.

Anal. Calcd. for $\text{C}_{29}\text{H}_{20}\text{N}_4\text{OCl}_3\text{SnMn}$: C, 48.34; H, 2.80; N, 7.78.

Found: C, 48.10; H, 2.74; N, 7.78.

Isolation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Br}$.

From a mixture of products formed by the reaction of $\text{Mn}(\text{CO})_5\text{Br}$ and $\text{C}_6\text{H}_5\text{NC}$, fractional crystallization using CHCl_3 -heptane resulted in the isolation of a small amount of dark orange rectangles which melt at 155-156 °C. The infrared spectrum is identical to that observed for other $\text{Mn}(\text{aryl isocyanide})_5\text{X}$ complexes.

Anal. Calcd. for $\text{C}_{35}\text{H}_{25}\text{N}_5\text{BrMn}$: C, 63.15; H, 3.80; N, 10.28.

Found: C, 64.50; H, 3.88; N, 10.75.

TABLE 1. INFRARED SPECTRAL DATA^a

Compound	$\nu_{C\equiv N}$	$\nu_{C\equiv O}$
$Mn(p-NO_2C_6H_4NC)_5Br$	2080s, 2050vs, 2000(sh)m	
$Mn(p-ClC_6H_4NC)_5Cl$	2060vs, 2000(sh)m	
$Mn(p-CH_3C_6H_4NC)_5Cl$	2060vs, 2020(sh)m	
$Mn(p-CH_3C_6H_4NC)_5Br$	2060vs, 2020(sh)m	
$Mn(C_6Cl_5NC)_5Br^b$	2070s	
$Mn(C_6H_5NC)_5Br, Cl$	2150w, 2050vs, 2000(sh)m	
$Mn(C_6H_5NC)_5CN$	2150w, 2050vs, 2000m	
$Mn(C_6H_5NC)_5SnCl_3$	2140w, 2050vs, 2000w	
$Mn(C_6H_5NC)_4(CO)SnCl_3$	2160w, 2090vs	1965m
$Mn(p-CH_3C_6H_4NC)_4(CO)Br$	2090vs, 2040(sh)w	1905m
$Mn(m-CF_3C_6H_4NC)_4(CO)Cl$	2090s, 2060s	1920m
$Mn(C_6H_5NC)_4(CO)Br$	2150w, 2090vs	1905m

a) IR spectra in CH_2Cl_2 solution; taken on Beckman IR-10.

b) Ref. 9.

TABLE 2. VOLTAMMETRIC DATA

Compound	$1/2[E_{p,c} + E_{p,a}]^a$	$ E_{p,c} - E_{p,a} ^c$	Process
Mn(p-NO ₂ C ₆ H ₄ NC) ₅ Br	0.62 1.29	120 mV 140 mV	+1 → +2 +2 → +3
Mn(p-ClC ₆ H ₄ NC) ₅ Cl	0.39 1.19	220 mV 240 mV	+1 → +2 +2 → +3
Mn(p-CH ₃ C ₆ H ₄ NC) ₅ Cl	0.22 1.13	200 mV 220 mV	+1 → +2 +2 → +3
Mn(p-CH ₃ C ₆ H ₄ NC) ₅ Br	0.25 1.15	210 mV 280 mV	+1 → +2 +2 → +3
Mn(C ₆ H ₅ NC) ₅ Br	0.32 1.17	65 mV 110 mV	+1 → +2 +2 → +3
Mn(C ₆ H ₅ NC) ₅ Cl	0.29 1.15	60 mV 65 mV	+1 → +2 +2 → +3
Mn(Cl ₅ C ₆ NC) ₅ Br	0.93	75 mV	+1 → +2
Mn(C ₆ H ₅ NC) ₅ CN	0.66 1.55	280 mV 200 mV	+1 → +2 +2 → +3
Mn(C ₆ H ₅ NC) ₅ SnCl ₃	0.86 1.62(E _{p,a}) ^b	90 mV	+1 → +2 +2 → +3

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CHARACTERIZATION AND REACTIVITY OF ISOCYANIDE COMPLEXES OF MANG--ETC(U)
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TABLE 2. (Contd.)

Compound	$1/2[E_{p,c} + E_{p,a}]^a$	$ E_{p,c} - E_{p,a} ^c$	Process
$Mn(C_6H_5NC)_4(CO)SnCl_3$	1.18 $1.80(E_{p,a})^b$	120 mV	+1 \rightarrow +2 +2 \rightarrow +3
$Mn(C_6H_5NC)_4(CO)Br$	0.76	140 mV	+1 \rightarrow +2
$Mn(p-CH_3C_6H_4NC)_4(CO)Br$	0.74 ^b	175 mV	+1 \rightarrow +2
$Mn(m-CF_3C_6H_4NC)_4(CO)Cl$	0.96 ^b	220 mV	+1 \rightarrow +2

- a) Average of cathodic and anodic peak potentials in volts vs saturated calomel electrode (aq. KCl); solutions in CH_2Cl_2 (5×10^{-3}) with $[N(C_4H_9)_4]ClO_4$ (0.1 M) as base electrolyte.
- b) Cathodic peak poorly defined or non-existent; generally a lower than expected current is observed.
- c) Criterion for electrochemical reversibility $|E_{p,c} - E_{p,a}| < 0.059$ v.

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CHARACTERIZATION AND REACTIVITY OF
ISOCYANIDE COMPLEXES OF MANGANESE
(Abstract)

By Hans Juergen Mueh

Under the supervision of Professor Paul M. Treichel, Jr.

The complexes $[\text{Mn}(\text{RNC})_6]\text{PF}_6$ ($\text{R} = \text{C}_6\text{H}_5$, $p\text{-CH}_3\text{C}_6\text{H}_4$, $m\text{-CH}_3\text{C}_6\text{H}_4$, $o\text{-CH}_3\text{C}_6\text{H}_4$, $p\text{-ClC}_6\text{H}_4$, $p\text{-BrC}_6\text{H}_4$, $p\text{-FC}_6\text{H}_4$, $p\text{-NO}_2\text{C}_6\text{H}_4$, $m\text{-CF}_3\text{C}_6\text{H}_4$, $p\text{-CH}_3\text{OC}_6\text{H}_4$, $p\text{-NCC}_6\text{H}_4$) were prepared by reaction of MnI_2 or $\text{Mn}(\text{CO})_5\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) with the free ligand. The $E_{1/2}$ values of the complexes for the $1e^-$ oxidation from $+1 \rightarrow +2$ were correlated with the Hammett σ_p of the substituent group and a correlation coefficient of 0.98 was obtained. Also, the invariance of $\nu(\text{CN})$ (2090 cm^{-1}) to the changes in σ_p or $E_{1/2}$ were rationalized on the basis of π -donation from the metal into a lowest unoccupied molecular orbital (LUMO) which is primarily phenyl ring in character.

Attempted oxidation of $\text{Mn}(\text{C}_6\text{H}_5\text{NC})_5\text{Cl}$ with AgPF_6 in THF resulted in the preparation of $[\text{Mn}(\text{C}_6\text{H}_5\text{NC})_6]\text{PF}_6$. The formation of this complex is due to halide extraction and dissociation of a solvent complexed intermediate supplying ligands to react with other intermediate species. The complex $\text{Mn}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})\text{Cl}$ reacted with AgPF_6 in a series of complexing solvents, resulting in the preparation of the complexes $[\text{Mn}(p\text{-CH}_3\text{C}_6\text{H}_4\text{NC})_4(\text{CO})(\text{L})]\text{PF}_6$ ($\text{L} = p\text{-CH}_3\text{C}_6\text{H}_4\text{NC}$, $\text{C}_5\text{H}_5\text{N}$, CH_3NC , $(\text{CH}_3)_3\text{CNC}$, and $o\text{-CH}_3\text{C}_6\text{H}_4\text{NH}_2$). A plot of $E_{1/2}$ vs $\nu(\text{CO})$

for these complexes produced a correlation coefficient of 0.99 and is consistent with the range of π -acceptor strengths of L.

The replacement of bromide ion in $\text{Mn}(\text{CO})_{5-n}(\text{CH}_3\text{NC})_n \text{Br}$ ($n = 2, 3, 4$) by CO and CH_3NC , accomplished in the presence of the halogen acceptors AlCl_3 (CO reactions only) or AgPF_6 , is found to be stereospecific, thus providing routes to the pure isomeric complexes cis- and trans- $[\text{Mn}(\text{CO})_2(\text{CH}_3\text{NC})_4]^+$, and fac- and mer- $[\text{Mn}(\text{CO})_3(\text{CH}_3\text{NC})_3]^+$. $E_{1/2}$ values for the isomeric species differ substantially. The qualitative explanation for this difference, involving relative stabilizations of the primarily non-bonding metal 3d orbitals through π -interactions with CO and CH_3NC , is justified by molecular orbital calculations.

Ultraviolet irradiation of $\text{CpMn}(\text{CO})_3$ in THF with excess isocyanide produced the complexes $\text{CpMn}(\text{RNC})_3$ ($\text{R} = \text{CH}_3, \text{C}_6\text{Cl}_5, \text{C}_6\text{H}_5, p\text{-ClC}_6\text{H}_4$). The cyclic voltammetry studies revealed a reversible current-potential curve for the process $+1 \rightarrow +2$ and only an oxidation peak for the process $+2 \rightarrow +3$. The $E_{1/2}$ values vary consistently with the known range of π -acceptor strengths of the isocyanides.

Reaction of $\text{Mn}_2(\text{CO})_{10}$ with $\text{C}_6\text{H}_5\text{NC}$ in refluxing THF yielded only the mono- and disubstituted species $\text{Mn}_2(\text{CO})_9(\text{C}_6\text{H}_5\text{NC})$ and $\text{Mn}_2(\text{CO})_8(\text{C}_6\text{H}_5\text{NC})_2$. Reaction of $\text{Mn}(\text{CH}_3\text{NC})_4(\text{CO})\text{Cl}$ with $\text{Mn}(\text{CO})_5^-$ yielded $\text{Mn}_2(\text{CO})_6(\text{CH}_3\text{NC})_4$. Reaction of $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})]^+$ with $\text{Mn}(\text{CO})_5^-$ yielded $[\text{Mn}(\text{CH}_3\text{NC})_5(\text{CO})][\text{Mn}(\text{CO})_5]$. Mass spectral studies on the neutral species showed evidence of stepwise loss of carbonyl, α -cleavage of the isocyanide, ligand rearrangement, and protonation of the complexed isocyanide.

The series of complexes $\text{Mn}(\text{CO})_{5-x}(\text{RNC})_x \text{X}$ ($\text{X} = \text{Cl}, \text{Br}; x = 4, 5$; $\text{R} = m\text{-CF}_3\text{C}_6\text{H}_4, p\text{-NO}_2\text{C}_6\text{H}_4, p\text{-ClC}_6\text{H}_4, p\text{-CH}_3\text{C}_6\text{H}_4, \text{C}_6\text{H}_5$), was examined electrochemically. The $E_{1/2}$ values again correlate with the σ_p of the substituent. The complexes $\text{Mn}(\text{C}_6\text{H}_5\text{NC}) \text{X}$ ($\text{X} = \text{Cl}, \text{Br}, \text{CN}, \text{SnCl}_3$) were also prepared and examined electrochemically. The $E_{1/2}$ values are consistent with the variation of electron withdrawing ability of the X group.

Approved Paul M. Treichel

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